

THE EFFECTS OF SCALE AND SPATIAL HETEROGENEITIES ON DIFFUSION IN  
VOLCANIC BRECCIAS AND BASALTS: AMCHITKA ISLAND, ALASKA

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A

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## ABSTRACT

Aqueous phase diffusion of molecules in fractured crystalline rock can play a dominant role in the fate and transport of contaminants, particularly if advective flows are very slow. The importance of the role of diffusion, typically a very slow process, also becomes an important mechanism to consider if the contaminants are long-lived in the subsurface, and thus their fate and transport must be considered over very long time-scales. Owing to the inherently heterogeneous nature of the subsurface, quantification of diffusive transport in the subsurface is extremely complex. The main objective of this study was to investigate the effects of the inherent heterogeneities of the subsurface on the diffusive transport of radionuclides, with a focus on the former underground nuclear test site at Amchitka Island, Alaska.

Commonly, the through-diffusion experiment is utilized to estimate transport parameters, the diffusivity and the effective porosity, for porous media samples. The available methods of mathematically deriving these parameters from these experiments are generally known to be subjective and unreliable. Thus, one phase of this study applied the results of through-diffusion experiments to investigate the applicability of the available solution methods to derive these parameters. The results indicated that a semi-analytical solution provided the most reliable parameter estimations. This knowledge was then applied to studies designed to understand the impacts of scale and spatial heterogeneities on diffusion at the study site. Multiple Amchitka Island core samples, both from the same and from various geologic layers, in varying sizes were analyzed in the laboratory via tracer-based and electrical methods, to quantify the diffusive properties and the effects of heterogeneities for Amchitka Island. The studies indicated that the transport properties for Amchitka Island are widely varying, by orders of magnitude, and are indicative of a geologically layered subsurface system; these results are extremely important for the long-term modeling of the fate and transport of radionuclides at Amchitka Island. Finally, in light of these studies, the question of long-term stewardship for the Amchitka Island test site was investigated and recommendations were provided, with the goal of providing an improved plan for the long-term monitoring and management of the site.

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## 1 INTRODUCTION

Amchitka Island, Alaska, was the site of three underground nuclear tests, which combined represent approximately 16% of the energy released during the entire US underground nuclear testing program. These tests were detonated between 1965 and 1971 by the former United States Atomic Energy Commission (AEC), now known as the US Department of Energy (DOE). They included the 80-kiloton Long Shot test, the 1-megaton Milrow test shot, and the 5-megaton Cannikin detonation, which, with an explosive yield of roughly 385 times that of Hiroshima, was the largest nuclear explosion ever detonated by the US (US Congress, 1989; Robbins, *et al.*, 1991; Norris and Arkin, 1998; DOE, 2006).

As a result of these nuclear tests, there is remaining concern regarding the possible migration of radionuclides released in the subsurface as a consequence of the explosions to the marine environment. In its responsibility for the protection of human and environmental health subsequent to its nuclear testing program, the DOE has developed a plan for the long-term surveillance and monitoring of the island (DOE, 2008). However, there are remaining concerns and uncertainties associated with this plan that still should be addressed (Benning, *et al.*, 2008). Owing to the complex nature of the island's subsurface, the relative remoteness of the island, and the lack of complete understanding of the subsurface effects of the detonations, a marine-based monitoring program has been planned rather than a traditional monitoring strategy for the island (terrestrial contaminant monitoring wells). For such a monitoring strategy, however, an understanding of the mechanisms controlling the transport of radionuclides through the Amchitka subsurface is essential. The results of previous fate and transport modeling efforts for the radionuclides potentially released in the subsurface have indicated that two of the key uncertainties in the groundwater models are the porosity and the intrinsic diffusion coefficient (Hassan, *et al.*, 2002). Thus, investigations designed at reducing these uncertainties are essential components in future evaluations of the risks associated with the site.

The fate and transport of contaminants through subsurface media characterized by consolidated fractured rock, as is found on Amchitka Island, is a complex problem. In this type of system, fractures serve as the primary flow pathways through the matrix rock. Contaminants, such as radionuclides, migrate with water contained in these fractures and then diffuse into the pore

spaces of the rock. In these systems, diffusion will continue into the matrix rock until concentrations in the groundwater in the fractures decrease to a level that will allow the radionuclides in the matrix rock to diffuse back into the fractures, thus remobilizing the contaminants. Due to the possible movement of radionuclides in and out of the matrix rock, matrix diffusion tends to dampen the maximum mass flux measured at any downgradient monitoring point. However, over long periods of time, diffusion processes alone will not decrease the overall mass moving downgradient. Thus, diffusion is often considered to be a retarding effect.

The diffusion flux rate in the rock matrix, known as the effective diffusion, is retarded, as compared to molecular diffusion, due to the properties of the rock. These properties include the extended travel length due to tortuous pathways within the rock, the fluctuating pore channel diameters, and the rock porosity. Amchitka Island is comprised of various layers of matrix rock, predominantly volcanic in origin. Thus, the effective diffusion for the island will vary spatially, due to heterogeneity in the type of rock encountered, as well as due to inherent heterogeneities within each category of rock. In the development of a monitoring plan for Amchitka Island, assessment of effective diffusion and its variability is vital to understanding and predicting the transport of radionuclides.

The spatial variability of the diffusive flux is an intuitive result of the heterogeneities within the rock. There is also potential variability in the diffusive flux due to the scale of measurement. A number of studies have been conducted to characterize the effective diffusion for various rock types at Amchitka Island; however these have generally been restricted to small-scale, laboratory studies, with diffusion measured through rock samples at the scale of centimeters. However, as the scale increases to field-scale studies, tests become increasingly restrained by both time and costs. Thus, there is a need to assess the predictive capabilities of the results derived from tests conducted on a centimeter scale to describe diffusion at larger scales.

The objectives of this doctoral research were to investigate the effects of scale and pore system connectivity on the intrinsic diffusion coefficient for volcanic matrix rock and to investigate the impacts of spatial heterogeneities, particularly in regards to highly heterogeneous breccias, on intrinsic diffusion coefficients. Since the results of these studies are important to the understanding of radionuclide transport through the subsurface at Amchitka Island, an associated

objective of this research was to assess the range of diffusivities found in the different rock types that comprise the subsurface of the island. Recommendations for radionuclide transport modeling are made in light of these effects. A final objective was to apply the knowledge gained through these investigations to an analysis of the long-term stewardship plan for Amchitka Island and to provide recommendations for improvement of the plan.

The results of these investigations are summarized in: Chapter 3, Comparison of Methods for the Determination of Diffusion Coefficients and Effective Porosities in Through-Diffusion Tests; Chapter 4, The Effects of Scale and Spatial Heterogeneities on Diffusion in Volcanic Breccias and Basalts: Amchitka Island, Alaska; and Chapter 5, Amchitka Island, Alaska: Moving Towards Long Term Stewardship. Each of these three chapters is either under review or has been accepted for publication in peer-reviewed journals: *Water Resources Research*, *Journal of Contaminant Hydrology*, and *Polar Record*, respectively, for the three chapters.

In Chapter 3, the investigations focused on a comparison of methods of analyzing typical laboratory diffusion experiments, with an emphasis on their respective abilities to derive reliable estimates of two important parameters for contaminant transport modeling, the intrinsic diffusion coefficient and the effective porosity. An important conclusion resulting from this investigation was that semi-analytical solution was the only method capable of providing a reliable estimate of the effective, or transport, porosity. The results of this investigation were then applied to analyze the results of laboratory experiments presented in Chapter 4.

In that portion of the research, it was found that for the Amchitka Island matrix rock, the pore-systems were found to be relatively well-connected, and the effects of scale were generally limited to lengths of 6 cm or less. An important conclusion from the study was that there is a potential for the estimated diffusivity to be misrepresented by an order of magnitude if multiple samples or longer sample lengths are not used. The large number of diffusivity measurements available from those investigations enabled an analysis of the probability distribution function (PDF) of the diffusivity, which had not been available in literature. It was found that PDF of individual lithologic layers generally followed a normal distribution, while the subsurface as a whole, including all of the layers, followed a lognormal distribution. Knowledge of the form of these PDF's is expected to enhance future stochastic modeling efforts.



The studies furthermore indicated that the diffusivities and porosities for the Amchitka Island rock varied widely, by greater than two orders of magnitude and more than 15%, respectively, thus indicating a strongly layered subsurface. Of particular concern for transport at Amchitka Island was the very low porosity and diffusivity of the andesite matrix rock, which is the media at the depth of the Long Shot test. These low values indicate a very low potential for retardation in this geologic media, while studies by Wagner (2007) indicated that layer as a preferential flow path for groundwater, due to its extensive fracture network. When the andesite sill layer at the Long Shot location was considered, the estimated travel time for groundwater breakthrough to the ocean floor was the shortest, an estimated 400 to 1400 years. If the impact of this shorter travel time is combined with the effect of the low potential for retardation, there is a concern that the radionuclides would not be significantly lowered from the groundwater transport rates, and the radionuclide travel could be significantly faster than predicted in other modeling efforts (Hassan, *et al.*, 2006).

The results of the experimental investigations were applied to the question of long-term stewardship for Amchitka Island. The DOE's plan for the long-term stewardship of the former nuclear test site are detailed in the 2008 report, "Long-term surveillance and maintenance plan for the U.S. Department of Energy Amchitka, Alaska, Site" (LTSMP). While a review of the LTSMP deemed the stewardship measures to be essentially protective of human and ecological health, there were significant remaining uncertainties identified at the site. These uncertainties include uncertainties with the groundwater and transport modeling, the potential for radionuclide release as a consequence of catastrophic events and/or island movement, and significant remaining biological uncertainties. As a consequence, a stronger commitment to future research to address these and a stronger commitment to oversight and review of the plan were recommended. To address these noted deficiencies in the LTSMP, the formation of a technical advisory panel was recommended.

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## 2 BACKGROUND

### 2.1 DIFFUSIVE TRANSPORT OF MOLECULES IN POROUS MEDIA

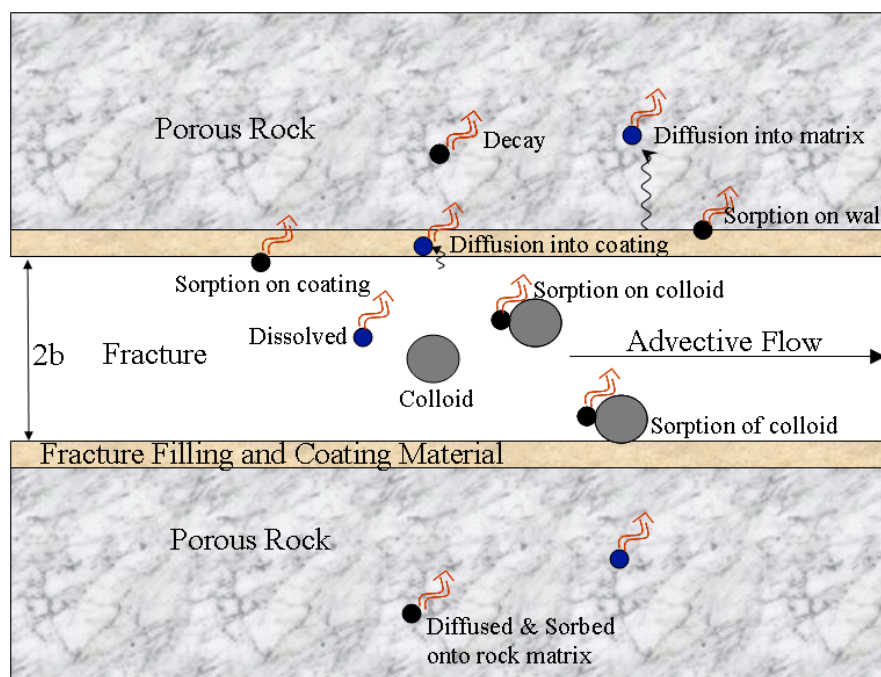
In porous media, such as fractured crystalline rock, the transport of contaminants through the subsurface system can become strongly controlled by the mass transport via diffusion of molecules from mobile water in a fracture into the matrix rock, as is described in Chapter 1. The conceptual model describing this process is described in the ensuing discussion, and the parameters used to describe the diffusion process in porous media are explained in detail.

#### 2.1.1 *Conceptual model for the diffusion from fracture networks into matrix rock*

In heterogeneous matrix rock, the diffusion of radionuclides or other contaminants from advective flow regimes in fractures into pore spaces in a matrix rock is a complicated phenomenon, as it is influenced by numerous chemical, physical, and biological processes occurring in the subsurface. Numerous researchers have developed models to describe the transport of molecules from a fracture into matrix rock (Neretnieks & Rasmuson, 1984; Lever, *et al.*, 1985; Rasmuson & Neretnieks, 1986; Parker & McWhorter, 1986; Yu, *et al.*, 1994; Tien & Li, 2001). These references include or exclude some of the influencing factors, based on the particular focus of the research. The models all describe the one-dimensional diffusional transport of molecules from a single, parallel-plate fracture, into a presumably homogeneous porous matrix. A summary of these conceptual models is included in the following, and illustrated in Figure 2.1.

In order to simplify the model, a number of assumptions must be made. The flow within the fracture is assumed to be advective, constant, laminar, and homogeneous, with complete mixing of the molecule and colloids within the fracture established due to transverse dispersion and diffusion. The fracture flow is also assumed to be much, much greater than flow in the rock matrix, such that flow in the matrix is negligible, and the primary transport mechanism within the matrix is diffusion. The length of the fracture is also assumed to be much greater than the fracture aperture,  $2b$  (see Figure 2.1). Both the fracture and the rock matrix are assumed to be completely saturated. Generally, sorption processes are assumed to be equilibrium, linear, instantaneous, and irreversible (Yu, *et al.*, 1994; Tien & Li, 2001). Colloids, particles with diameters between 1 nm and 1000 nm, are transported within a fracture at a flow rate greater than

that of an average water molecule, because colloids are restricted to the faster flowing water in the center of a fracture. Due to their size, colloids are excluded from the porous matrix (Tien & Li, 2001). As illustrated in Figure 2.1, the processes which affect the flow and transport of a chemical, in this case, radionuclides, in this model include (Neretnieks & Rasmuson, 1984; Neretnieks, 1993; Yu, *et al.*, 1994; Tien & Li, 2001): (1) the advective transport of water containing dissolved phase radionuclides within a fracture, (2) attachment of radionuclides onto colloidal particles, which are transported by advection in the fracture, (3) sorption of radionuclides onto fracture walls, (4) sorption of colloids with attached radionuclides onto fracture walls, (5) diffusion of sorbed radionuclides along fracture walls, termed surface diffusion, (6) diffusion of radionuclides through fracture filling and coating materials, if present, on the walls of the fracture, (7) diffusion of radionuclides from the fracture into the pore spaces of the rock, (8) sorption of diffused radionuclides onto surfaces within the porous matrix, and (9) decay of radionuclides in all of the transport phases.



**Figure 2.1** Illustration of processes included in a conceptual model for radionuclide transport in a fractured porous rock.

In addition to these processes, Moridis (1999) also distinguishes between mobile and immobile phases of pore waters, where the immobile phase exists as a thin film surrounding the porous media grains. In this case, diffusion, sorption, and decay processes are also defined for the mobile and immobile pore waters. However, due to the assumption that flow within the porous media is so slow as to be negligible, these processes are neglected and all of the pore waters are considered to be immobile.

Various other chemical and physical factors have potential to impact these processes. Temperature will affect the rates of diffusion. Redox conditions, pH, and complexation will impact the solubility and sorption properties, and thus, also the transport properties of radionuclides (Neretnieks, 1993). Also, diffusion properties are generally measured in laboratory experiments, in low concentration solutions. The presence of other ions, at potentially high concentrations in salt water, will result in electrochemical effects on diffusion parameters (Snyder, 2000). Research has shown that overburden pressures will affect the porosity and effective diffusion coefficients (Skagius & Neretnieks, 1986b). At a site-scale, the types of rock encountered will vary, and thus both the physical and chemical properties affecting flow and transport will vary. However, even on the scale of a single fracture, there is evidence to suggest that both the porosity and effective diffusion coefficient will decrease with distance from the fracture, with the magnitude of the decrease depending on the degree of weathering in the rock matrix, such that there is a “zone of enhanced mobility” surrounding the fracture (Skagius & Neretnieks, 1986a; Bradbury & Green, 1985; Heath, *et al.*, 1992). Neretnieks (1993) indicates that the fracture aperture of a single fracture may vary by several orders of magnitude at the site-scale.

Diffusional transport may also be affected by the presence of dead end pores in the rock matrix. Lever, *et al.* (1985) analyzed the impacts of dead-end pores on diffusion in porous media. The dead end pore model developed addressed some of the discrepancies found in early-time data from laboratory through diffusion experiments versus simple Fickian theory applied to the steady-state region. The results indicate that the simple Fickian theory applied to steady state provides an adequate estimate of diffusion parameters when the length of the dead end pores is small in comparison to the length of diffusion (i.e. length of sample). The authors estimated that this occurs at a scale of approximately 5 cm. While, in practice, this negligible dead end pore length is rarely achieved in laboratory experiments performed on thin slices of rock (and due to time

constraints), this is theoretically easily achieved at the site scale, where distance between fractures, for granites is on the order of 10 m. Thus, Lever, *et al.* (1985) estimated that there will be little impact of dead end pores when modeling diffusion on the site scale.

For three dimensional modeling of flow and transport in fractured rock, information on the fracture density, fracture porosity, fracture apertures, spacing between fractures, intersections, as well as lengths and orientations would contribute to the model. A simplified approach to 3-D modeling would assume isotropic, heterogeneous conditions with a fracture network comprised of regularly shaped cubic blocks, and such models have been presented in literature (Neretnieks & Rasmuson, 1984; Rasmuson & Neretnieks, 1986; Parker & McWhorter, 1986). A network of irregularly shaped and sized blocks becomes significantly more difficult to model. Such a model would become far more complex due to the fact that the physical and chemical properties influencing transport are often neither heterogeneous nor isotropic. Often the information on fracture networks required to model is not available (Neretnieks, 1993).

Neretnieks and Rasmuson (1984) developed a 3-D radionuclide transport model. For a fracture network comprised of equally-sized, cubic blocks, they present a simple relationship between fissure aperture,  $b$ , fissure spacing,  $S$ , and flow porosity,  $\phi_f$ :

$$b = \frac{S\phi_f}{3} \quad (2.1)$$

They also developed a method to examine a fracture network comprised of irregularly shaped and sized blocks through the use of “pseudobodies” in the 3-D model. Rasmuson & Neretnieks (1986) analyzed the impacts of factors influencing the transport of radionuclides in a fractured rock system. Using the method of pseudobodies, they determined that, as compared to other unknowns, the simplification of a 3-D fracture network comprised of irregular blocks to a cubic network is minimal. However, according to Neretnieks (1993), the size of the 3-D blocks is an important factor with regards to the storage capacity of the rock for the radionuclide for a given contact time.

### 2.1.2 Diffusion coefficients

In studies involving the examination of diffusion coefficients of porous solids, it is important to identify the application of relevant parameters. Many researchers define various diffusion

coefficients and associated parameters differently, and thus it becomes important to clarify definitions (Walter, 1984; Bradbury & Green, 1985; Shackelford, 1991). The primary difference in diffusion coefficient definitions by various researchers in geologic, hydrologic, and soils science literature is the inclusion or exclusion of a porosity term in Fick's first and second laws and subsequent exclusion or inclusion, respectively, of a porosity term in the definition of an effective diffusion coefficient. Though these two diffusion coefficients are obviously different, in literature, often both are referred to as the "effective diffusion coefficient," leading to confusion when comparing the results of various researchers (Feenstra, *et al.*, 1984; Bradbury & Green, 1985; Skagius & Neretnieks, 1986a; Glass & Buenfeld, 1998; Lü & Ahl, 2005). Furthermore, results are often presented in terms of the diffusion coefficient (Feenstra, *et al.*, 1984; Glass & Buenfeld, 1998; Lü & Ahl, 2005), which is a property of the porous media, as well as the diffusing molecule, and so when different molecules are employed as tracers in experiments, the literature often lacks a standardized method of presenting results, such as expressing results in terms of the formation factor rather than as effective diffusion coefficients, which would avoid confusion and improve the ability to compare and incorporate results of various researchers for modeling purposes. However, this too is subject to some interpretation, as noted in Snyder (2001), because it requires knowledge of the molecular diffusion coefficient for a particular molecule under the specific conditions of the test. The reported molecular diffusion coefficients values for various molecules available in literature are typically given for "infinitely dilute solutions," a condition which may not be relevant for a particular through-diffusion experiment.

Fick's first law describes the diffusional flux of molecules due to Brownian motion in the presence of a concentration gradient. However, when diffusion occurs through a porous media, the flux is slowed from the molecular, or free water, diffusion rate due to the properties of the porous medium, and an effective or intrinsic diffusion coefficient ( $D_i$ ) is applied to describe the change to the flux. The one-dimensional molecular flux per unit area of the porous medium,  $J_x$ , can be expressed as:

$$J_x = -D_i \frac{\partial C}{\partial x} \quad (2.2)$$

Where  $C$  is the concentration of the diffusing molecule in the pore water and  $x$  represents distance. The flux described here is through the porous medium; the intrinsic diffusion

coefficient describes the flux averaged across the total cross-sectional area of the porous medium and thus includes the influence of the porosity of the medium and is a function of the porous medium, the solution, and the diffusing molecule. Fick's second law describes the rate of change of the flux across the medium. The concentration rate change for a porous medium is adjusted for the fact that the concentration per unit area is only contained in the pore waters and incorporates a molecular "sink" or sorption term. In literature, Fick's second law appears in one of two forms (Bradbury & Green, 1985; Glass & Buenfeld, 1998; Grathwohl, 1998; Moridis, 1998):

$$\alpha \frac{\partial C}{\partial t} = D_i \frac{\partial^2 C}{\partial x^2} \quad (2.3)$$

$$R \frac{\partial C}{\partial t} = D_p \frac{\partial^2 C}{\partial x^2} \quad (2.4)$$

In Equation (2.4),  $D_p$  considers that the flux across the porous medium will only occur within the pore spaces of the medium and is equal to  $D_i$  divided by the effective porosity,  $N_e$ . The rock capacity factor is  $\forall$  and  $R$  is the retardation coefficient. These are expressed as:

$$\alpha = \phi + \rho_b K_d \quad (2.5)$$

$$R = 1 + \frac{\rho_b}{\phi_e} K_d \quad (2.6)$$

The bulk dry density of the medium is  $\rho_b$  and  $K_d$  describes a linear equilibrium sorption. The bulk porosity, and differences between  $N$  and  $N_e$  will be discussed in the succeeding. These forms of Fick's Law (Equations 2.3 and 2.4) are limited to consideration of sorption as (1) linear, (2) instantaneous, and (3) irreversible (Moridis, 1999).

In Equation (2.4), if the porosity is considered equivalent to the effective porosity,  $D_p$  is equivalent to  $D_i$  divided by the porosity, and  $R$  is equal to  $\forall$  divided by the porosity, and thus Equations (2.3) and (2.4) are equivalent. However, there is confusion in the literature in that both  $D_i$  and  $D_p$  are often referred to by the same term, the "effective diffusion coefficient." Furthermore, there is some discrepancy between porosity values applied to these equations; this discrepancy will be discussed more fully in the following. In Bradbury & Green (1985), the term,



$D_p$ , is referred to as the pore water diffusion coefficient, which is probably a more appropriate term.

In some of the literature (Feenstra, *et al.*, 1984; Kunetz & Hench, 1998; Lü & Viljanen, 2002; Lü & Ahl, 2005), the solution to Fick's second law is applied to model the results of laboratory diffusion experiments in the absence of distinguishing the effects, or potential effects, of sorption. With this treatment, Fick's second law is written as:

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} \quad (2.7)$$

Where  $D_a$  is the apparent diffusion coefficient. Additional confusion occurs when this term is sometimes also referred to as the “effective diffusion coefficient.” To be consistent with Equation (2.3), the apparent diffusion coefficient is (Bradbury & Green, 1985; Moridis, 1998):

$$D_a = \frac{D_i}{\alpha} = \frac{D_i}{\phi + \rho_b K_d} = \frac{D_p}{R} = \frac{D_p}{1 + \frac{\rho_b}{\phi_e} K_d} = \frac{\phi_e D_p}{\phi(1 + \rho_b K_d)} \quad (2.8)$$

When the molecule is conservative, i.e. no sorption occurs, then  $K_d = 0$ , and  $D_a$  is equal to  $D_i$  divided by porosity or  $D_a$  is equal to  $D_p$ . The various forms expressed in Equation (2.8) are only valid if the bulk porosity is equal to the effective porosity. This discrepancy in interpretation will be discussed in the following section.

### 2.1.3 Intrinsic diffusion coefficient

The intrinsic diffusion coefficient can be expressed in terms of the properties of the diffusing molecule, solvent, and porous medium, which all theoretically influence its value. Van Brakel and Heertjes (1974) proposed a definition whereby the intrinsic diffusion coefficient ( $D_i$ ) is related to effective porosity ( $N_e$ ), constrictivity ( $\delta$ ), and tortuosity ( $\tau$ ) as:

$$D_i = D_m \left( \frac{\phi_e \delta}{\tau^2} \right) = D_m F_f \quad (2.9)$$

where  $D_m$  is the molecular diffusion coefficient, or the coefficient of diffusion in free water. It is noted that the porosity term used in the preceding refers to the transport, or effective, porosity, to

the exclusion of porosity resulting from dead-end and unconnected pores, and is different from the bulk porosity,  $N$ . The quantity,  $N_e \delta / \tau^2$ , referred to as the formation factor,  $F_f$ , can be used to characterize the porous media (Bradbury & Green, 1985; Skagius & Neretnieks, 1986a) and can be derived from through diffusion experiments and knowledge of the molecular diffusion coefficient.

The justification for the exclusion of porosity in the diffusion coefficient and subsequent use of the pore water diffusion coefficient in Equation (2.4) is the consideration of the porosity as a measurable parameter (Shackelford, 1991). However, this generally precludes experimental evidence that indicates that not all of a porous medium's pore spaces are available for through transport (Bradbury & Green, 1985; Lever, *et al.*, 1985; Skagius & Neretnieks, 1986a). There are several causes for the differences between transport and bulk porosities. An immobile thin film may exist surrounding particle grains due to adhesive forces. Highly structured, inaccessible, water may also occur in interlayers of clay minerals. Also, dead end and unconnected pores may occur, particularly in fractured rock (de Marsily, 1986; Fetter, 1994; Grathwohl, 1998). Grathwohl (1998) explains difficulties that may arise in measuring the porosity of very dense, low porosity rocks such as granites using the water saturation method. When the total quantity of water retained in the rock is very low, surface effects, such as the draining of large pores or retention of small amounts of water on the rock surface, can be significant. Complete water saturation may not be achieved, and this would be difficult to assess. Furthermore, a small value of the rock capacity, as with very low porosity rocks or/and low sorption can lead to large errors in  $\alpha$ , and subsequently, large errors in the laboratory-determined apparent diffusion coefficient.

In order to examine some of these potential differences in porosities, Lever, *et al.*, (1985) proposed an analysis of through diffusion data that includes "dead end pore theory." However, analysis determined that for most through diffusion experiments, the exclusion of dead end pore theory is adequate. This conclusion is however, dependant on the specific nature of the pore structure for the studied porous medium. Although in Moridis (1999), the effective diffusion term does not include the porosity term, his model does incorporate the influences of the immobile thin film, with regards to its impacts on solubility and sorption. There is a notable difference between the application of the effective versus bulk porosity by different researchers to transport modeling with Fick's Laws. Moridis (1999) considers the effects of a reduced porosity

to pertain to all of the transport mechanisms, i.e., the “accessible” porosity is applied to both the sorption and diffusion portions of Equation (2.4). Other researchers (Bradbury & Green, 1985; Skagius & Neretnieks, 1986a; Grathwohl, 1998) apply the effective porosity only to the diffusion phenomenon, while applying the bulk porosity to the sorption phenomenon. There is logic to both approaches, but the application depends on the nature of the differences between the effective and bulk porosities for the specific porous medium. If a portion of the pore waters are considered inaccessible due to adsorption onto mineral surfaces and/or inclusion into interlayers of clays, i.e., leading to an immobile thin film, then both diffusion and sorption phenomena will be constrained by this inaccessibility. However, if the cause of the inaccessibility is unconnected pores, then sorption would not be affected, as these pores would still act as a “sink” for molecules, while the diffusional transport would be constrained. Since these effects occur on the pore scale, it is difficult to assess with current technology which interpretation is more appropriate.

#### *2.1.4 Formation factor*

Further differences are noted in the literature regarding definitions and applications of the formation factor, tortuosity, and constrictivity, and thus some clarification on these parameters as considered in this research is warranted. As noted in Equation (2.9), the definition of the formation factor employed herein is equal to the ratio of the effective diffusion coefficient to the molecular diffusion coefficient, as in Klinkenberg (1951). Thus, the formation factor will have values less than one, as the flux of a solute through a porous media will be much slower than the flux of a solute in free water. Other researchers (Charbeneau, 2000; Snyder, 2001) utilize a formation factor term which is defined as the reciprocal of this, and thus report values greater than one. The formation factor applied herein is the first one, having a value less than one, since logically it can be thought of as a factor which describes how the flux of a molecule is slowed from free water by the properties of the porous medium.

## **2.2 THE ROLE OF DIFFUSION IN LONG-TERM STEWARDSHIP AT AMCHITKA ISLAND**

Consideration of the effects of diffusion on the fate and transport of contaminants in the subsurface is important at sites where the advective flow is very slow. This occurs at sites, such as Amchitka Island, where the subsurface flow system consists of fractured bedrock. Though advective flow through a fracture system is slow, the half-lives of several key radionuclides are

long, and thus, when stewardship of the site is considered, the fate and transport of contaminants must be modeled over very long time-scales. Over these long time scales, diffusion becomes an important mechanism to consider in the long-term fate of contaminants (Neretnieks, 1980). The role that diffusion will play in the transport of radionuclides is a key premise regarding the safety of underground nuclear detonations. It is presumed that radionuclides will be safely contained within the matrix rock at a site, due to the compounding effects of very slow advective flow, retardation through diffusion and sorption, and decay of radionuclides, and thus that the likelihood of release to the environment via subsurface flow will be minimal.

Studies into subsurface flow in fractured rock have shown that the main flow paths are along flow-scale fractures (Lever, *et al.*, 1985; Neretnieks, 1993). On the microscopic scale, however, the matrix rock is comprised of microfractures which define the boundaries between crystals. Though very small, these microfractures are still much larger than molecules. Water, referred to as pore water, is contained within these networks of microfractures. Though the permeabilities in matrix rock are so low as to be considered negligible and water is considered essentially immobile, connected pore waters will still allow the transport of contaminant molecules through the process of diffusion. Overall, the volume of the pore water is much, much greater than the volume of water in the fractures, and thus, there is a great potential for the storage of molecules within the matrix rock. The surface area of the microfractures will also be much greater than the surface area of the flow-scale fractures, yielding an even greater storage potential for molecules that are strongly sorbed onto crystalline surfaces (Neretnieks, 1980, 1993).

There is ample literature which indicates that under slow advective flow conditions, such as exist in fine-grained soils, diffusion can become a dominant process in contaminant transport (Goodall and Quigley, 1977; Desaulniers *et al.*, 1981, 1982, 1984, 1986; Crooks and Quigley, 1984; Johnson *et al.*, 1989; Shackelford, 1991). Similarly, Neretnieks (1993) has shown that over long time scales, matrix diffusion of radionuclides into dense crystalline rock will often become a more important factor in the spreading of a contaminant plume than mechanical dispersion. When long “contact times” are considered, the transport rate of water at a site may actually have negligible impact on the transport rate of a solute at that same site, since the transport of the solute will be more influenced by the ratio of the water transport rate to the diffusion and sorption capacity of the rock (Neretnieks, 1980; Neretnieks, 1993). For a strongly sorbed molecule, when long term fate and transport is considered, diffusion will have an important impact. For

nonsorbing molecules, such as tritium, the transport will also be considerably slower than that of water at long time scales, due to diffusion in and out of pores (Lever, *et al.*, 1985; Neretnieks, 1993).

The importance of continued research into diffusion of radionuclides in fractured rock for long-term stewardship has been expressed by Neretnieks (1993). The author notes that historically, research for sites involving radionuclide transport have been largely focused on hydraulic and geologic influences on groundwater transport, and that “very little of that information” has been able to be applied towards the estimation of radionuclide migration. However, there is still a general lack of knowledge regarding such influences are diffusion and channeling, which will play a large role in the transport of the radionuclides.

Research into the fate and transport of radionuclides at Amchitka has demonstrated the importance of the assessment of diffusion in the rock matrix to long-term stewardship. Hassan, *et al.* (2002) produced a model to describe Amchitka Island’s groundwater flow and the transport of radionuclides released during the Long Shot, Milrow, and Cannikin tests. The purpose of the report was to provide radionuclide transport times required to assess the potential risks to human health and the environment posed by the release of radionuclides during the three tests. The risk assessment includes a conceptual and a numerical model of groundwater flow and a conceptual and numerical model for contaminant release and transport. These incorporate geologic, hydrologic, and chemical data. Because much of this information is uncertain, the report also includes sensitivity analysis in order to ascertain the relative significance of these uncertainties. The analyses reveal that one of the key uncertainties in the prediction of radionuclide transport is the matrix diffusion coefficient. The significance of this parameter will depend on the half-life of individual radioactive components as well as modeled flow velocities (Hassan, *et al.*, 2002).

The groundwater travel times in the Long Shot test vicinity have been estimated by Wagner (2007). The results of modeling suggest that the groundwater travel time from the shot cavity to the estimated point of discharge on the seafloor ranges from 1,000 to 3,300 years. However, an alternative model considers the influence of a geologic feature with enhanced hydraulic conductivity, namely an andesite sill that is present at the depth of the detonation. When the influences of the andesite sill are incorporated into the model, the results suggest a greatly reduced travel time of 500 years. No estimates of radionuclide travel times are reported.

However, it is likely that radionuclide travel will be significantly retarded as compared to groundwater travel, due to diffusion and sorption processes. It is noted that while the andesite sill exhibits enhanced hydraulic conductivity, most likely due to an extensive fracture network, estimates of the diffusion coefficient for an andesite sample recovered from the vicinity of the Milrow test shot area indicate a much lower matrix porosity and effective diffusion coefficient (1 to 2 orders of magnitude less than that of basalts and breccias at the island) than in other stratigraphic layers present on the island. If there is less diffusion into the matrix rock in this layer, then theoretically, this will result in less retardation of the radionuclides with respect to groundwater flow, and radionuclide travel times will be impacted.

### 2.3 PHILOSOPHY OF LONG-TERM STEWARDSHIP

At many DOE sites throughout the United States, technologic and economic limitations prevent cleanup activities from achieving a state that would allow unrestricted access and use of the site in a manner which would still ensure the health and safety of current and future generations. For some sites, particularly those that are a legacy of the DOE nuclear weapons programs, the nature of the contaminants themselves inhibits feasibility of remediation. Many radionuclides, for example, have very long half-lives and thus are very persistent in the environment; furthermore, many decay into radioactive daughter products that also pose health hazards. For these sites, the DOE implements “long-term stewardship” or “long-term management,” a plan of actions designed to minimize current and future human health risks associated with remaining (residual) contamination at these sites (USDOE, 1999; USDOE, 2001). Several groups provide information and recommendations as to how long term stewardship should be handled at these sites, such as the USDOE (USDOE 1999; USDOE 2001), the National Research Council (NRC) (NRC 2000), and the State and Tribal Government Working Group (STGWG) (STGWG 1999). Others provide additional discussions and recommendations regarding long term stewardship as well, such as Burger (2000), Burger (2001), and Burger and Gochfeld (2001).

The term “stewardship” is defined by the DOE as “activities necessary to maintain long-term protection of human health and the environment from hazards posed by residual radioactivity and chemically hazardous materials (STGWG, 1999). In practice, this entails all of the activities required to ensure the protection of human health and the environment for a site after remediation is “complete,” economically and technically feasible options for remediation are exhausted, or further remedial options would present increases in risks to human health (USDOE, 1999).

According to DOE's stewardship documents, LTS activities encompass: the operation, maintenance, and monitoring of engineered remediation and/or containment systems; ensuring the maintenance and effectiveness of physical controls, such as fences and barriers, and institutional controls, such as ordinances, building permits, deeds, and easements; other monitoring and maintenance activities, as required; information management and dissemination; maintaining stakeholder relations and involvement; and preparing budgets. In addition to these activities, the DOE maintains a commitment to the "protection of natural resources, protection of cultural resources, and a variety of other environmental, social, economic, and engineering issues" as important aspects to LTS plans (USDOE, 1999; USDOE, 2001).

In the context of these listed activities, DOE also recognizes the complexity of maintaining a site under the status of stewardship over the time frames required for radionuclides. Political and cultural priorities will likely shift over time, as will personnel and data management systems. The availability and certainty of funding is also a critical issue regarding LTS. Furthermore, the state of scientific knowledge and technical capabilities are also likely to change with time, such that some of the uncertainties regarding the fate and transport of contaminants at sites will be increasingly addressed and options for feasible remediation may be developed. In order to address the later issues, DOE recommends frequent review and reiteration of LTS plans, as well as general support for research and development. In order to address issues of changing populations and cultural values, DOE recommends "frequent communication across parties at each site." Furthermore, DOE acknowledges that "education and training will be a critical part of long-term stewardship, particularly among affected parties, and will serve to continually reinforce concepts and keep the concepts familiar and pertinent (USDOE, 2001)."

The National Research Council (NRC) reviewed DOE's stewardship and long-term management policies and published the results of their independent study in 2000 (NRC, 2000). The list of activities critical to stewardship are similar to those expressed by DOE, however, NRC is far more emphatic in its expression of the concerns over factors related to the long-term effectiveness of stewardship as a means to protect human health and the environment. Amongst the concerns are the lack of proven reliability of institutional controls, issues of over continued reliance on funding from congressional appropriations for stewardship activities, fallibility of land-use restrictions (the Love Canal Superfund site is a historic example of this fallibility) over the time-scales required, and the lack of scientific and technical understanding of contaminant fate and

transport in the subsurface. NRC states that, “...the working assumption of DOE planners must be that many contamination isolation barriers and stewardship measures at sites where wastes are left in place will eventually fail, and that much of our current knowledge of the long-term behavior of wastes in the environmental media may eventually be proven wrong. Planning and implementation at these sites must proceed in ways that are cognizant of this potential fallibility and uncertainty (NRC 2000, p.5).”

In addition to the stewardship activities listed by the DOE, the NRC indicated that stewardship activities should also include the support of “research and development aimed at improving basic understanding of both the physical and sociopolitical character of site environments and the fate, transport, and effects of residual site contaminants.” DOE (1999, 2001) did acknowledge this need, though in a more equivocal manner, and not at the site level specifically. NRC cites the examples of the Idaho National Engineering Lab (INEL) and the Nevada Test Site (NTS) as examples of cases where the transport of radionuclides in the subsurface has been shown to be dramatically faster than had been predicted in models, demonstrating the consequences of relying on simplified fate and transport models for complex, multi-scalar, heterogeneous subsurface conditions and the needs for further research. Acknowledging that years of research will be required to increase scientific knowledge for many issues as they relate to risks associated with the sites, NRC recommends that, in the preparation of long-term institutional management plans, “scientific, technical, and organizational deficiencies or knowledge gaps should be acknowledged frankly, and where possible, research investments should be made to correct them (NRC, 2000).”

In order to address some of these issues, NRC recommends that long-term management plans for sites should include *redundancy* in entities implementing and managing plans, to counteract the inherent fallibility in reliability, and *layering*, or the use of more than one means of institutional control to accomplish the same goal. They recommend that periodic review and reevaluation of management systems should occur at 5-year intervals, the same as is required for sites under the EPA Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), though it is noted that this stipulation will not necessarily lead to the implementation of these reviews, as evidenced by the extreme backlog of CERCLA 5-year reviews (NRC, 2000). This iterative process of implementation, reevaluation, and revision is also emphasized in the recommendation on long-term stewardship of the National Conference of State Legislatures, State and Tribal Government Working Group (STGWG, 1999).



## 2.4 HEALTH EFFECTS OF RADIONUCLIDES

There are two categories of health effects associated with exposure to radiation: deterministic and stochastic. Deterministic effects are generally associated with high exposure over short periods of time, and result in the inability of a cell, or an organ, to function. Deterministic effects have an associated threshold dose. Stochastic effects, which include cancer, are defined by a probability that an effect will occur. Generally, in risk determinations when radiation exposure is considered, the no threshold rule is applied (Cooper, *et al.*, 2003).

Radiation exposure at very high levels can cause death or serious detrimental effects to organs and tissue. At low dose levels, radiation can cause “somatic malignancies and hereditary effects attributable to cell transformations.” These effects are random, or stochastic, but because of them, when human health risks are concerned, the “no threshold” dose theory is commonly applied. This theory considers the idea that there is no threshold dose below which there will be no risk of health effects. The linear no-threshold hypothesis assumes that increases in risk are proportional to increases in dose (IAEA, 1998a). The most radioactive nuclides are those with short half-lives, and thus health risks are associated with exposure at shorter time periods. Long lived nuclides emit very little radiation, but may pose a health risk if they are present in the body (Cooper, *et al.*, 2003).

In general, the health hazards associated with a radionuclide depend on the type of radiation emitted and the specific activity. There are three types of radioactive emissions that are produced during the decay of a radionuclide: alpha and beta particles and gamma rays. Alpha radiation essentially is comprised of helium ions and is largely emitted during the radioactive decay of transuranics. Alpha particles are characterized by a high linear energy transfer (LET) rate, and are not very penetrating in skin and tissue. However, once ingested or inhaled into the body, damage to cells and tissue in the vicinity can occur from alpha radiation. Beta particles, which are comprised of energetic electrons, also have a high LET and are only slightly more penetrating than alpha particles. Beta radiation may be absorbed in only the first few millimeters of skin or tissue and therefore poses limited external exposure risks, however, poses a similar threat to alpha particles once incorporated into the body. Gamma radiation is comprised of high frequency electromagnetic radiation. Gamma rays have a very low LET rate, and are very penetrating, and

therefore are of concern with regards to external exposure (Robbins, *et al.*, 1991; Klaassen, 1996).

Once a release occurs, the fate of the nuclide in the environment, as well as factors pertaining to the behavior and distribution within the body affect the radiotoxicity of a nuclide (IAEA, 1998a). With regard to atmospheric nuclear testing and accidents from reactors, both long-lived and short lived radionuclides may pose potential health risks. In general, due to retention underground, the list of radionuclides of concern in underground nuclear tests should be limited to the longer-lived nuclides, since short-lived nuclides will decay prior to a release to the environment. An additional factor to consider is the likely partitioning of these radionuclides into lava, rubble, gas, and water. Those partitioned largely on the lava will be less mobile as the lava will become solidified and resistant to chemical leaching. Radionuclides partitioned onto the rubble surfaces will be more mobile, as they are more susceptible to leaching. Highly soluble radionuclides, such as tritium, will exist almost entirely in the water (IAEA, 1998b).

In the event of atmospheric testing or accidental releases from reactors, doses of radionuclides to the public that are of concern are often associated with fallout. According to the International Physicians for the Prevention of Nuclear War (IPPNW), the contaminants posing significant health risks from fallout are: the short lived radionuclides zirconium-95, cerium-144, and ruthenium-106; the intermediate-lived radionuclides cesium-137 ( $^{137}\text{Cs}$ ) and strontium-90 ( $^{90}\text{Sr}$ ); and the most toxic of the long-lived radionuclides, plutonium-239 ( $^{239}\text{Pu}$ ) (Robbins, *et al.*, 1991).

With regards to underground testing, the advisory committee of the International Atomic Energy Agency, IAEA, produced a list of radionuclides posing potentially significant health risks and likely to exist in the subsurface at the French atolls as a result of underground nuclear testing. Their list was produced by survey of the Evaluated Nuclear Structure Data File (ENSDF) produced by the Brookhaven National Laboratory and revised January 31, 1996. There are 2000 radionuclides known to man. Of these, there are 124 that have half lives between 1 and ten billion years, which is the criterion set by the IAC as posing a potential health risk. 40 of these are likely to be produced in an underground nuclear explosion, as a result of one of the following six categories of production: residues of fuel materials, reaction products of fuel materials, fission products, activation products of non-fuel bomb materials, activation products in stemming (filling) materials and rocks surrounding the explosion, and activation products of neutron fluence

detectors (IAEA, 1998b). It is presumed that the general list of radionuclides potentially produced from other underground nuclear tests should be similar; however, specific differences are possible due to the type of nuclear device detonated, the background conditions, and the size of the explosion.

The inventory produced by IAEA for the French Atolls, by category is summarized in the following. Radionuclides existing as residues of fuel materials include: tritium ( $^3\text{H}$ ); Weapons Grade Plutonium (WGP), comprised of  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{241}\text{Pu}$ , and their daughter products, uranium-236 ( $^{236}\text{U}$ ), americium-241 ( $^{241}\text{Am}$ ), neptunium-237 ( $^{237}\text{Np}$ ),  $^{233}\text{U}$ , and thorium-229 ( $^{229}\text{Th}$ ). The radionuclides produced from the reactions of fuel materials include: tritium, uranium-239, 240, and 241, as well as uranium-236 and 237 and plutonium-238, and their decay products, plutonium-239, 240, and 241, neptunium-237, uranium-233 and thorium-229. In the category of fission products are: selenium-79 ( $^{79}\text{Se}$ ), krypton-85 ( $^{85}\text{Kr}$ ), strontium-90 ( $^{90}\text{Sr}$ ), zirconium-93 ( $^{93}\text{Zr}$ ), Niobium-93m ( $^{93\text{m}}\text{Nb}$ ), technetium-99 ( $^{99}\text{Tc}$ ), ruthenium-106 ( $^{106}\text{Ru}$ ), palladium-107 ( $^{107}\text{Pd}$ ), cadmium-113m ( $^{113\text{m}}\text{Cd}$ ), tin-121m, 126 ( $^{121\text{m}}\text{Sn}$ ,  $^{126}\text{Sn}$ ), antimony-125 ( $^{125}\text{Sb}$ ), iodine-129 ( $^{129}\text{I}$ ), cesium-134, 135, 137 ( $^{134}\text{Cs}$ ,  $^{135}\text{Cs}$ ,  $^{137}\text{Cs}$ ), promethium-147 ( $^{147}\text{Pm}$ ), samarium-151 ( $^{151}\text{Sm}$ ), and europium-155 ( $^{155}\text{Eu}$ ). The activation of non-fuel bomb materials produces: cobalt-60 ( $^{60}\text{Co}$ ), chlorine-36 ( $^{36}\text{Cl}$ ), nickel-63 and 59 ( $^{63}\text{Ni}$ ,  $^{59}\text{Ni}$ ), lead-205 ( $^{205}\text{Pb}$ ), and iron-55 ( $^{55}\text{Fe}$ ). Radionuclides will be produced from the activation of stemming materials and rocks surrounding the explosion: chlorine-36 ( $^{36}\text{Cl}$ ), calcium-41 ( $^{41}\text{Ca}$ ), potassium-40 ( $^{40}\text{K}$ ), iron-55 ( $^{55}\text{Fe}$ ), and europium-152 and 154 ( $^{152}\text{Eu}$ ,  $^{154}\text{Eu}$ ). If incorporated in the test, there also could be activation products of neutron fluence detectors, however, these generally have half-lives less than one year, and thus were not considered (IAEA, 1998b).

The health risks posed by most of these radionuclides result, if exposure or ingestion occurs, from the risks associated with the type of radioactivity released from their decay – alpha particles, beta particles, or gamma particles. With alpha emissions, reproductive, carcinogenic, and developmental effects are known to occur (UNSCEAR, 1982; NRC, 1988). However, some radionuclides specifically pose health risks, primarily due to their behavior once incorporated into the body. These are discussed in the following.

Plutonium-239 is a highly radioactive alpha-emitter and is highly toxic, even though, in general, it is likely to only be released in small quantities (Robbins, *et al.*, 1991). Its daughter products

decay with emissions of alpha, beta and gamma rays. However, because it emits no gamma rays directly, health risks are associated with ingestions and inhalation. Plutonium-239, once incorporated into the body, tends to be concentrated in the lungs, liver, or skeleton. Because it is not otherwise expelled from the body and because its decay, with a half life of approximately 90 years, is very slow, it will continue to emit radiation in the tissues of the body for many years. Cancers and immune system suppression occur in laboratory animals exposed to plutonium-239 (ATSDR, 1990). Studies by U.S. and Russia into the effects of chronic exposures to Pu-239 over long time periods, both internally deposited and externally deposited have indicated cases of “chronic radiation sickness,” pneumosclerosis, respiratory disease. In cases of acute radiation, pulmonary fibrosis and fatalities are documented (Seligman, 2000).

Americium-241, with a half-life of 432 years, releases primarily alpha radiation when it decays and is a low-level emitter of gamma radiation. Because it is a low-level gamma emitter, external exposure risks are low, however, there are significant risks associated with internalized americium. Because of its long half life and tendency for retention in the bones, stochastic effects, including the risks of bone cancers, are of concern. However, with regards to underground releases, it is noted that americium tends to be highly sorbed to soil particles (ATSDR, 2004a).

Cesium-137 is considered a radionuclide of intermediate half-life, 30 years. Decay of radioactive cesium produces beta and gamma radiation, and thus there are significant health risks both from external and internal exposures. Internal exposures have largely been associated with contamination of food. In the environment, cesium is capable of traveling very far in air, it is highly soluble in water, and is strongly sorbed to soils. The Chernobyl accident contributed significant worldwide deposition of radioactive cesium, which accumulated on moss and lichen in arctic environments. It then accumulated in reindeer, caribou and livestock, and has been found in breast and pasteurized milk. When incorporated into the body, cesium tends to accumulate in soft tissues. Cesium has been associated with fetal damage and effects on brain development (ATSDR, 2004b; Kohlhoff, 2002).

Strontium-90, like radioactive cesium, is an intermediate half-lived nuclide, with significant associated health risks. It has a half-life of 29 years and emits beta particles when it decays. In the environment, it is highly water soluble and is fairly mobile in the subsurface due to much

lower sorption than cesium. Because it is a beta emitter, external exposures can cause radiation damage to skin. When ingested, strontium tends to accumulate in the intestines; however, some strontium will still enter the bloodstream, where it is of specific concern because there it behaves like calcium and will be uptaken into bones. Once uptaken in the bones, decay will slowly emit radiation, which damages bones and cells in surrounding tissue. Strontium-90 is linked to leukemia, and causes cancers of bone, nose, and lung in laboratory animals (ATSDR, 2004d; Kohlhoff, 2002).

Iodine-131 decay emits gamma radiation, and thus poses health risks from external radiation, primarily associated with atmospheric testing and accidents. It has a short half-life of 8 days, so aside from venting, it is generally not considered to be a threat when releases are in the deep subsurface, as is the case with underground nuclear testing. Radioactive iodine accumulates in soil, where it then interacts with organic matter and can be uptaken by plants. From there, grazing animals can ingest it, and it becomes concentrated in milk, whereby it is transferred to humans, specifically children, who consume greater quantities of milk than adults. Once iodine-131 is in the body, it behaves as nonradioactive iodine, and is uptaken by the thyroid glands, where it has shown to disrupt the production of thyroid hormones or cause cancer to develop. In children, this is particularly dangerous, since the thyroid glands are essential to growth and development, and the size of the glands yields a higher dose of radioactive iodine (IAEA, 1998a; Klaassen, 1996; ATSDR, 2004c). A US-Russian study into the effects of nuclear releases in Russia's Southern Urals documented thyroid disorders in children living in the vicinity who were exposed to iodine-131 (Seligman, 2000).

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### **3 COMPARISON OF METHODS FOR THE DETERMINATION OF DIFFUSION COEFFICIENTS AND EFFECTIVE POROSITIES IN THROUGH-DIFFUSION TESTS**

#### **Abstract**

Diffusion coefficients and effective, or connected, porosities are important parameters in the assessment of the fate and transport of contaminants when advective flows are low to negligible. The through-diffusion experiment is commonly employed in laboratory studies to estimate these two important parameters; however, it has been widely recognized that the derived estimates of the effective porosities are subjective and unreliable. This unreliability largely arises from the applied method of solution to Fick's Law of diffusion for the through-diffusion experimental data. Commonly in literature, the time-lag solution method is employed to analyze transient-state experimental data. This study presents and discusses various solutions, analytical and semi-analytical, to Fick's Law for the through-diffusion experiment, and applies these solutions to the results of three through-diffusion experimental data sets, conducted on samples with order of magnitude differences in diffusivities. For each experiment, the derived intrinsic diffusion coefficients and effective porosities for each method are compared. It was shown that while there is little difference between methods in the derived intrinsic diffusion coefficients, the semi-analytical solution provides an improved method for reliably estimating the effective porosity from through-diffusion experimental data.

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### 3.1 INTRODUCTION

Consideration of the effects of diffusion on the fate and transport of contaminants in the subsurface is important in porous media when advective fluxes are low to nonexistent. Diffusion can become the dominant transport mechanism sites where the subsurface media is comprised of fractured rock or clays or within engineered containment and barrier systems. The diffusion processes in fractured rock, in particular, have been the subject of many studies, as this media is suggested for the long-term storage of nuclear wastes. Others have indicated that the connectivity and availability for transport of the pore system of a rock will strongly influence the retardation of radionuclides through diffusion processes (Löfgren & Neretnieks, 2006). At Amchitka Island, Alaska, a former underground nuclear test site and the subject of this study, the porosity and the intrinsic diffusion coefficient have been shown to be two of the key uncertainties in fate and transport modeling efforts for the site (Hassan, *et al.*, 2002). These parameters were measured for two predominant Amchitka Island rock types in this study using a common experimental technique. The analysis of the results using three different solutions to Fick's Law is discussed. To further the discussion on the different solutions to Fick's Law, the test and analysis was repeated for a manufactured porous plate.

There is ample experimental evidence that indicates that not all of a porous medium's pore spaces are available for through transport (Bradbury & Green, 1985; Lever, *et al.*, 1985; Skagius & Neretnieks, 1986). Several causes are responsible for the differences between transport and bulk porosities. An immobile thin film may exist surrounding particle grains due to adhesive forces (the diffuse double layer). The influences of this adhesion have been shown to be solute-dependant, as in the case of anion exclusion (Schön, 1996; Van Loon, 2003; Appelo & Wersin, 2007). Highly structured, inaccessible water may also occur in interlayers of clay minerals. Furthermore, dead-end and unconnected pores may occur, particularly in fractured rock (de Marsily, 1986; Fetter, 1994; Grathwohl, 1998; Reimus, *et al.*, 2007). Additional unconnected pores may be caused by the introduction of microfractures in sample extractions, either through drilling or cutting. These have been shown to penetrate up to 1 cm into a sample, though generally most of the effects are seen in the outer few millimeters (Autio, *et al.*, 1999; Löfgren & Neretnieks, 2006). However, despite the importance of the effective porosity to modeling efforts, there remains no generally accepted experimental method to estimate this parameter.

The application of the through-diffusion method has been well established in literature as a method for measuring the intrinsic diffusion coefficient of a porous media (Feenstra, *et al.*, 1984; Bradbury & Green, 1985; Skagius & Neretnieks, 1986; Gilling, *et al.*, 1987; Snyder, 2001; Lü & Viljanen, 2002; Witthüser, *et al.*, 2003). In a typical through-diffusion test, two cells are separated with a porous media sample centered between the two cells. One cell contains an initial concentration of a tracer, while the other cell is initially tracer-free. The intrinsic diffusion coefficient is estimated by measuring the flux of tracer through the porous sample over time, as described by Fick's Laws of Diffusion. Theoretically, the effective, or transport, porosity can be derived from the early-time, or transient-state, data from a through-diffusion experiment, though there is much debate over the accuracy of these derived effective porosities (Grathwohl, 1998; Van Loon, *et al.*, 2003; Appelo & Wersin, 2007; Motellier, *et al.*, 2007). Some of this difficulty arises from the method of estimation of the effective porosity from through-diffusion experimental data. Because there is no analytical solution available for Fick's Law to determine the intrinsic diffusion coefficient for the application of the through-diffusion experiment, numerous approximate solutions have been explored in the literature (Crank, 1975; Bradbury & Green, 1985; Lever, *et al.*, 1985; Skagius & Neretnieks, 1986; Kirchner & Nageldinger, 1996; Moridis, 1999; Snyder, 2001). All of these solutions are approximations based on assumed boundary conditions. The purpose of this paper is to compare various methods available to determine diffusion coefficients and effective porosities from through-diffusion experiments and to discuss the results of applications of these methods to experimental results.

This study includes the analyses of the various solution methods to the results of through-diffusion experiments, using iodide as a conservative tracer, on three different samples of consolidated porous media. The intrinsic diffusion coefficients for the three media represent order of magnitude differences (intrinsic diffusion coefficients on the order of  $10^{-10}$  m<sup>2</sup>/s,  $10^{-11}$  m<sup>2</sup>/s, and  $10^{-12}$  m<sup>2</sup>/s) with corresponding measured bulk porosities of 40.9%, 16.8%, and 13.7%, respectively. The experimental durations were 45 days, 78 days, and 365 days, with increasing duration for slower diffusive flux rates. The receiving cells were sampled frequently during each experiment, allowing the uncertainties associated with measured tracer quantities due to sampling and instrument error to be reduced through the application of relatively large data sets. The source cell tracer concentrations were also monitored throughout the duration of the experiments, allowing verification of the boundary conditions assumed in the model applications.

### 3.2 THEORY AND METHODS

Fick's first law describes the diffusional flux of molecules due to Brownian motion in the presence of a concentration gradient. When diffusion occurs through a porous media, the flux is slowed from the molecular, or free water, diffusion rate due to the properties of the porous medium (and the solute for some media), and an effective or intrinsic diffusion coefficient ( $D_i$ ) is applied to describe the change to the flux. Fick's second law describes the rate of change of the flux across the medium (Bradbury & Green, 1985; Glass & Buenfeld, 1998; Grathwohl, 1998; Moridis, 1998):

$$\alpha \frac{\partial C}{\partial t} = D_i \frac{\partial^2 C}{\partial x^2} \quad (3.1)$$

The rock capacity factor,  $\alpha$  is:

$$\alpha = \phi + \rho_b K_d \quad (3.2)$$

Ideally, for the case of a conservative diffusing molecule, the sorption coefficient,  $K_d$ , will be equal to zero, and  $\alpha$  will be equal to the porosity. The solution in this form is limited to consideration of sorption as (1) linear, (2) instantaneous, and (3) irreversible (Moridis, 1999).

The intrinsic diffusion coefficient can be expressed in terms of the properties of the diffusing molecule, solvent, and porous medium, which all theoretically influence its value. Van Brakel and Heertjes (1974) proposed a definition whereby the intrinsic diffusion coefficient ( $D_i$ ) is related to the molecular diffusion coefficient and the effective porosity ( $\phi_e$ ), constrictivity, and tortuosity of the porous medium as:

$$D_i = D_m \left( \frac{\phi_e \delta}{\tau^2} \right) = D_m F_f \quad (3.3)$$

The quantity,  $\phi_e \delta / \tau^2$ , referred to as the formation factor,  $F_f$ , can be used to characterize the porous media (Bradbury & Green, 1985; Skagius & Neretnieks, 1986) and can be derived from through-diffusion (TD) experiments and knowledge of the molecular diffusion coefficient. Though the formation factor can be a useful parameter to describe differences between the

transport properties of various porous media, it is subject to some interpretation, as noted in Snyder (2001), because it requires knowledge of the molecular diffusion coefficient for a particular molecule under the specific conditions of the test.

Many solutions to the diffusion equation, Equation (3.1), are proposed in literature (Carslaw & Jaeger, 1959; Crank, 1975) for different geometries and boundary conditions. Some of these solutions as applied to the through-diffusion experiment are presented and discussed in the following. For all of the solutions, both the source and receiving cells are assumed to be completely mixed, such that samples are representative of concentrations at the  $x = 0$  (source, concentration  $C_S$ ) and  $x = L$  (receiving, concentration  $C_R$ ) faces. As presented, all of the methods consider a sample and receiving cell that are initially tracer-free, i.e.  $C(x \geq 0, t = 0) = 0$  and  $C_R(t = 0) = 0$ .

### 3.2.1 Time-lag method

The time-lag (TL) analytical solution, published by Carslaw and Jaeger (1959) and by Crank (1975), considers a porous slab at steady-state ( $\partial C / \partial t = 0$ ). The boundary conditions for the steady-state solution to (2), include the assumption that the source concentration,  $C_s$ , at any time is constant and that it is much greater than the receiving cell concentration,  $C_S \gg C_R$ , at all times. Furthermore, this assumption implies that after an initial transient-state, the concentration changes in both cells are negligible (Glass & Buenfeld, 1998).

The solution for the receiving cell concentration takes the form (Crank, 1975; Bradbury & Green, 1985; Skagius & Neretnieks, 1986; Witthüser, *et al.*, 2003):

$$C_R = \frac{ALC_S}{V_R} \left[ \frac{D_i t}{L^2} - \frac{\alpha}{6} - \frac{2\alpha}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{D_i n^2 \pi^2 t}{L^2 \alpha}\right) \right] \quad (3.4)$$

At large times, the last term approaches zero, so the solution can be simplified as:

$$C_R = \frac{ALC_S}{V_R} \left[ \frac{D_i t}{L^2} - \frac{\alpha}{6} \right] \quad (3.5)$$

Linear regression on the straight line portion of the time-concentration data allows  $D_i$  and  $\alpha$  to be estimated from the slope and intercept, respectively, from Equation (3.5). On a graph of receiving cell concentration versus time, the slope of the straight line portion yields an estimate of  $D_i$  and the intercept on the time-axis yields  $\alpha$  (or  $\phi_e$  for a conservative tracer). Thus, the determination of both the intrinsic diffusion coefficient and the effective porosity from the experimental data is possible, noting the difficulties with low porosity rocks as previously discussed (Grathwohl, 1998). Once  $D_i$  and  $\alpha$  (equal to  $\phi_e$  for a conservative tracer) have been determined from Equation (3.5), these parameters can be applied to Equation (3.4) to compare the model to the entire experimental data set, thus including the pre-steady state time period.

This solution has the advantage of a direct calculation of the effective diffusion coefficient and rock capacity factor. However, the choice of “steady-state,” and thus the determination of the slope and intercept, is somewhat subjective (Moridis, 1999), though the daily incoming flux method, described in the subsequent, and/or the use of statistical methods can be applied to alleviate this subjectivity. Another limitation to the solution is the requirement of constant source concentration. In many applications of the through-diffusion technique, this condition may be violated. It requires experimental design to ensure that this condition is achieved (Lü & Viljanen, 2002; Lü & Ahl, 2005; Van Loon, 2003), or at minimum, verification of this condition through sampling. Moridis (1999) provides examples demonstrating the potential errors that would arise if this condition is violated. Grathwohl (1998) discusses other limitations of the time-lag method, particularly when applied to cases with low porosity media or highly sorbing tracers.

### 3.2.2 Daily incoming flux method

The daily incoming flux (DIF) method is considered as a subset of the time-lag method, since the parameters,  $D_i$  and  $\phi_e$  are either derived using the time-lag method or an alternative formulation of Equation 4. The incoming flux at the receiving cell ( $x = L$ ) side of the sample is (Motellier, *et al.*, 2007):

$$J_x(x = L, t) = D_i C_s \left[ \frac{1}{L} + \frac{2}{L} \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{D_i n^2 \pi^2}{\alpha L^2} t\right) \right] \quad (3.6)$$

A graph of the flux,  $J$ , versus time can be used to visually ascertain the duration of the steady-state period (Van Loon, *et al.*, 2004); however, the application of this method requires knowledge



of the parameters  $D_i$  and  $\alpha$ , and therefore an iterative solution is required. Since this solution is derived using the same boundary conditions as the time-lag solution, it is subject to the same limitations as the TL method.

### 3.2.3 *Semi-analytical solution*

Moridis (1998, 1999) proposes a semi-analytical (SA) solution to Fick's Law (Equation 3.1) based on numerical inversions of Laplace transformations. In recognition of the potential for violation of the two key limiting assumptions of the TL solution, namely, the assumption of a constant source cell concentration and the assumption that the source cell concentration at all times is significantly greater than the receiving cell concentration, Moridis proposed his semi-analytical solutions so that a changing source cell concentration can be considered. As a result of this consideration, the solutions are significantly more complex, however, the FORTRAN codes developed to obtain the semi-analytical solutions have been made available by Moridis at the URL: <http://esd.lbl.gov/Diffusion/> (last accessed by the author June, 2008). The complete solutions are found in Moridis, 1998 and Moridis, 1999.

In its complete form, the solution includes consideration of the effects of decay, sorption, mobile and immobile pore water, and surface diffusion. Sorption is considered to be linear in all cases, however, equilibrium, kinetic, and irreversible cases are included in the solution. Since through-diffusion tests typically utilize a stable, conservative diffusing molecule, and because no information is normally available on the mass transfer between mobile and immobile phases of pore water, only bulk parameters are included, and the problem for through-diffusion testing is simplified to the form as presented in Equation (3.1).

In addition to the boundary conditions described for all of the methods, the conservation of mass yields another boundary condition:

$$M_S + M_W + M_F + M_R = V_S C_{S0} \quad (3.7)$$

The final boundary condition equates the mass of the diffusing molecule that crosses the  $x = L$  boundary to the mass of the molecule in the receiving cell (Moridis, 1998, 1999):

$$-A \int_0^t \left[ D_i \left( \frac{\partial C}{\partial x} \right)_{x=L} \right] dt = V_R C_R \quad (3.8)$$

While the SA solution provides the ability to incorporate data from both the receiving and source cells, to use the data from both cells, there may be practical limitations due to the chemical analysis methods employed. Some chemical analysis methods may provide a higher degree of accuracy in measurements at relatively high concentrations, as are likely to be present in the source cell, while other methods may provide improved measurements in the lower concentrations, as are likely to be present in the receiving cell. It is not likely that any analytical method will provide the same degree of accuracy in the measurement of both cells, unless the concentrations in both cells are relatively close in magnitude, which would result in excessive experimental duration for low diffusivity media.

This SA model, in its complete form, is the most robust of the models, in terms of its consideration of a suite of complex phenomena which will influence fate and transport of contaminants in porous media by diffusion and diffusion/sorption interactions. Technological limitations at present time limit the ability to assess all of these parameters. There is also some question over the application of the effective porosity to both diffusion and sorption influences, as the analyses by others (Bradbury & Green, 1985; Skagius & Neretnieks, 1986) do not consider the effective porosity to influence sorption. Without future investigations into the pore scale structure of porous media and interactions on this scale, discussions on this issue are limited to the theoretical. The tradeoff to the complexity provided by this model is that this method requires history matching techniques to derive parameters (intrinsic diffusion coefficient and effective porosity) rather than direct calculation, though algorithms to reduce the tediousness of this process are available (Thomas & Hellums, 1972).

#### 3.2.4 *Approximate analytical solution*

Lü and Viljanen (2002) and Lü and Ahl (2005) present an approximate analytical (AA) solution that is a “special case” of the solution presented by Moridis (1999). Similar to the Moridis’ solution, this solution is derived using inversion of a Laplace transformation of Fick’s Law. These authors’ approach, similar to the time-lag solution, is limited to the case of constant source concentration, i.e.  $C(x=L, t \geq 0) = C_s$ . The boundary condition expressed in Equation (3.8) is applied. The solution for the receiving cell concentration is expressed as:

$$C_R(t) = C_s \left( 1 - \exp\left(-\frac{t}{d}\right) \right) \quad (3.9)$$

Where  $d$  is:

$$d = \frac{V_R L}{\phi A D_a} + \frac{L^2}{2 D_a} = \frac{V_R L}{A D_i} + \frac{\phi L^2}{2 D_i} \quad (3.10)$$

This method has an advantage in that it does not require that the steady-state condition is achieved. With added model complexity, this method also requires history-matching, rather than direct determination of the diffusion coefficient. This model does not appear to be applicable for the determination of the effective porosity, as will be noted in the Discussions section.

### 3.3 EXPERIMENTAL METHODS

#### 3.3.1 Samples

Three consolidated porous media samples were examined in this study: two breccia samples, denoted as Core 19 and Core 24, from Amchitka Island, Alaska, and one manufactured porous plate. The breccia samples were derived from drill hole UAe-1 on Amchitka. Core 19 was obtained from a depth between 1412 m to 1414 m (4632 – 4640 ft) below grade, and is described as “breccia, greenish-black, very dense, brittle, altered. Matrix contains small (<12 mm) aphanitic basalt fragments. Zeolites and chalcedony distributed throughout; some pyroxene crystals in matrix (Gard, *et al.*, 1969a).” Core 24 was obtained from a depth between 1593 – 1596 m (5227 – 5237 ft), and is described as “Breccia, mottled pale-green and very light gray, propylitized. Lithic fragments range in size from 1 mm to 3 cm and are subrounded to rounded, predominantly basalt. Fine-grained clayey matrix, constitutes about 10 percent of rock and contains rare pyroxene crystals (Gard, *et al.*, 1969b).” Both breccia core samples were cut with a diamond saw for use in the through-diffusion reactors; and prior to diffusion experimentation, each sample was prewashed in three changes of deionized water, then dried and saturated with deionized water under vacuum pressure (-40 to -50 kPa) to determine bulk porosities via the water saturation method. The samples are shown in Figure 3.1 and their sizes are summarized in Table 3.1.

The manufactured porous plate (PP), manufactured by Refractron Technologies Corp, is designed to have a uniform pore size. It is comprised of approximately 86%  $\text{Al}_2\text{O}_3$  and 10%  $\text{SiO}_2$  and 4% other materials. The measured bulk porosity by water saturation was 38.8%. Reconstruction and analysis of 3-D images of the sample produced by X-ray computed tomography (CT) scans yield

a porosity of 40.9%. The average pore size for the sample is 61 microns, as measured by a sphere packing algorithm (Skyscan, 2007). The discrepancy between the measured and CT-calculated bulk porosities is likely caused by the drainage of surface pores in the water saturation method, indicative of the difficulties in accurately measuring porosity via the water saturation method. The sample dimensions are indicated in Table 3.1.

### 3.3.2 *Experimental*

Through-diffusion experiments, as described in the literature (Bradbury & Green, 1985; Skagius & Neretnieks, 1986; Snyder, 2001), using iodide as a conservative tracer, were conducted on the three different samples of consolidated porous media. The through-diffusion reactors (Figure 3.2) were constructed of acrylic and the rock was affixed using Lexel® caulk, which adheres well to wet and porous materials.

Prior to affixing the samples to the acrylic plates, samples were oven-dried and allowed to cool. In each test on the breccia samples (Figure 3.2a), the receiving cell was filled with the receiving cell solution ( $\text{NaNO}_3$  solution, Table 3.1) and ample time, based on conservative estimates of flow using measured sample permeabilities and visual observations, was allowed for the samples to achieve saturation. At time zero, the source cell was filled with the source cell solution ( $\text{NaI}$  solution, Table 3.1). The experimental procedure was altered for the PP sample in order to prevent advective flow in this high porosity sample. For the PP sample diffusion experiment (Figure 3.2b), deionized water was added to the receiving cell and allowed to flow through to the source cell to achieve sample saturation; one day was allowed to ensure hydrostatic equilibrium, and the source and receiving cells were simultaneously spiked with sodium iodide and sodium nitrate (Table 3.1), respectively. In all three experiments, hydrostatic pressures were balanced on source and receiving cell sides of the sample; in the tests on the breccia samples, this balance was accomplished by adjusting the volumes to account for solution density differences, while for the PP sample test, solutions with equal densities were chosen. Membrane behavior has been observed in concrete and clays (Zhang & Buenfeld, 1997; Malusis & Shackelford, 2002), and therefore, for the breccia samples, solutions were chosen to balance the osmotic pressures on either side of the sample (Bradbury & Green, 1985; Skagius & Neretnieks, 1986). Osmosis is not a consideration for the PP sample due to its relatively large pore size and the use of dilute solutions for the TD experiment.

For all experiments, magnetic stir bars were used at slow revolutions to mix both the source and receiving cells. The experiments were conducted at nearly constant temperatures of  $21\pm1^{\circ}\text{C}$ ,  $23\pm0.5^{\circ}\text{C}$ , and  $25\pm0.5^{\circ}\text{C}$ , for the Core 19, Core 24, and PP samples, respectively. Throughout the duration of the experiments, samples of both the source and receiving side were collected. Each time a sample, 5 mL in volume, was removed, 5 mL of source and receiving cell solutions were replaced, appropriately. The iodide concentrations in the stock source solutions were monitored over the course of the experiment; no oxidation or decay of iodide was detected. The details for each experimental setup are summarized in Table 3.1.

Samples were analyzed for iodide via ion chromatography (IC). The chromatography apparatus is a Dionex AS40 Autosampler with an AS-11 Analytical Column and an AG-11 Guard Column. Sodium bicarbonate, 1.0 mM, is used as an eluent. The method detection limit was 2 ppm (mg/L) for the Core-19 through-diffusion experiment; IC analytical methods were modified and the method detection limit for the other two experiments was 0.5 ppm. Calibration checks were performed routinely using both internal and external sources and sampling was performed in duplicate periodically. The maximum analytical error was determined to be 6%. Dilutions are required for concentrations greater than 100 mg/L, and the dilution technique error is 2-3% for the 1:400 dilutions required for the breccia source cell samples to fall within the mid-calibration range. Duplicate or triplicate dilutions were performed for each sample requiring dilution to reduce this error; however, instrument error still applies, and the effect of this is magnified with increasing dilutions. Additionally, replicate samples were collected, representing approximately 10% of the total samples, in order to assess sampling error. This was found to be less than 0.1%.

### 3.4 RESULTS

The experimental data for the receiving cell iodide concentrations and the source cell iodide concentrations for each experiment are illustrated in Figures 3.3–3.5 and 3.6-3.8, respectively. The time-lag (TL), semi-analytical (SA), approximate analytical (AA), and finite-difference (FD) models were applied to analyze the experimental data and to determine the intrinsic diffusion coefficients and effective porosities. The best-fit model, as determined by residual sum of squares, for each method is illustrated in Figures 3.3, 3.4, and 3.5. For the TL method, the duration of the steady-state period was visually verified by graphing the daily incoming flux (DIF) using the TL-derived intrinsic diffusion coefficient and effective porosity; then an iterative

process was used to match the steady-state period for the derivation of the parameters to the steady-state period using the DIF. The daily incoming fluxes for each experiment, applying the parameters derived from the SA model, are illustrated for each experiment in Figures 3.3, 3.4, and 3.5; the resulting graphs indicate the steady-state period. For the PP sample, because the TL and AA solutions only apply to the constant source concentration boundary condition, only the data up to day 10 are included in the calculations; at this point, the source cell concentration had decreased by only 4%.

Only the semi-analytical method predicts changes in the source cell concentrations, and the source cell concentrations for the best-fit effective diffusion coefficient to the receiving cell data is shown in Figures 3.6, 3.7, and 3.8. For the TD experiments on the breccia samples, the measurement errors in the source cell are greater in magnitude than the actual changes in concentration; thus, the source cell concentrations can only be used for a visual check of the SA model predictions. It appears, from Figures 3.6, 3.7, and 3.8, that the source cell concentrations predicted by the SA models are in good agreement with the measured concentrations for all three experiments. The agreement between the source cell concentrations and model predictions also provide evidence that there is no detectable oxidation or decay of iodide during the course of the experiments.

The derived intrinsic diffusion coefficients, formation factors, and effective porosities (for all but the AA method) for each sample using each solution method are summarized in Table 3.2. The formation factor is calculated by dividing the intrinsic diffusion coefficient by the molecular diffusion coefficient for iodide, at the appropriate temperature for each experiment. The molecular diffusion coefficient of  $2.048 \times 10^{-9} \text{ m}^2/\text{s}$  at  $25^\circ\text{C}$  applied was calculated using the Wilke and Change Equation (Treybal, 1980) for the average experimental temperatures of  $21^\circ\text{C}$  and  $23^\circ\text{C}$ , with published parameters (CRC, 2008). Since the experiment involves the diffusion of iodide into a salt solution ( $0.1 \text{ M NaNO}_3$ ), it is possible that there may be electrochemical effects that would alter the molecular diffusion coefficient; however, a study by Stokes, *et al.* (1957) examined the effects of salt solutions on the molecular diffusion of iodide and reported little differences for salt solutions under  $1 \text{ M}$ . Similar results are indicated by Snyder (2001). The effect of counter-diffusion of nitrate in these systems is analogous to the electrochemical effects. This phenomenon can effectively be described by a reduction in the molecular diffusion coefficient from that of the ion in an infinitely dilute solution; for iodide in a  $0.1 \text{ M}$  solution,

which is the maximum ionic strength used in this study, the potential decrease is estimated to be less than 10% (Cussler, 1984; Daniel & Albright, 1991). However, in perspective, Cussler (1984) notes that published molecular diffusion coefficients are known to only be accurate to within 5-10%.

The effective porosities of each sample (Table 3.2) were determined from the transient-state period (Figures 3.10, 3.11, 3.12). For the TL method, the effective porosity, or  $\alpha$ , was determined from the intercept on the time-axis (Equation 3.4). In the SA method, a history-matching technique was used to derive the effective diffusion coefficient and the effective porosity by providing the best-fit model for experimental data, discussed in the following. For the AA method, the model was found to be insensitive to changes in the porosity, and thus, the derivation of the effective porosity by history-matching is not possible. To highlight the differences between the bulk porosity and effective porosity for the Core 19 sample, Figure 3.9 illustrates the best-fit models applying the bulk measured porosity, while Figure 3.10 illustrates the best-fit models using a derived effective porosity. The Core 24 and PP sample results do not show substantially different effective and bulk porosities (given in Tables 3.2 and 3.1, respectively).

For each method, the determination of the best-fit model is judged by the least mean square prediction error, or residual sum of squares (RSS). Uncertainties in the derived parameters are estimated through a combination of the empirical and modeling approaches described by Eurachem (2000, 2007). The analytical errors on individual measurements are random in nature and associated uncertainties in derived parameters based on these are reduced by the contribution of the large number of data points to the reduction of the standard deviation from each model fit. The largest contribution to the uncertainties results from the relatively large analytical errors associated with the source cell concentration. According to Nugue, *et al.* (2007), estimates of the effective diffusion coefficients derived from steady-state analyses on through-diffusion experiments are  $\pm 10\%$ ; the uncertainty analyses for this study indicate estimates within that range.

### 3.5 DISCUSSION

As indicated in Table 3.2, for the breccia samples, the estimated intrinsic diffusion coefficients for each method are within the ranges of uncertainties, indicating no substantial difference

between the derived intrinsic diffusion coefficients for the various methods. For the PP sample, the TL solution indicates an intrinsic diffusion coefficient that is slightly higher than that estimated with the SA solution, considering the uncertainties associated with each. The deviation is caused by a violation of the constant source concentration (4% decrease) and the influence of a greatly reduced number of samples considered in the solution due to the steady-state boundary condition required by the TL method. However, even with a 4% change in the source cell concentration, both the TL and AA solutions provide reasonable estimates of the intrinsic diffusion coefficient, in comparison to that derived by the SA solution. It is noted that for a high porosity and high diffusivity sample, the constant source concentration can be difficult to maintain, and thus, in this case, the SA solution is likely more appropriate.

For the Core 19 and Core 24 samples, the effective porosities derived from the through-diffusion experimental data (for the SA method) are less than the bulk measured porosity, though the effect is greater in the Core 19 sample. This result can at least partially be explained by the issues noted by Grathwohl (1998) in estimating porosities by the water saturation method, particularly with regards to low porosity samples. First, because in the water saturation method, the infiltration of water occurs in 3-dimensions, it does not necessarily correlate to a porosity that is available for through-transport. Also, when the total quantity of water retained in the rock is very low, surface effects, such as the draining of large pores or retention of small amounts of water on the rock surface, can be significant. Lastly, complete water saturation may not be achieved, and whether it is achieved would be difficult to assess (Grathwohl, 1998).

Another important cause for a discrepancy is likely due to the influence of unconnected pores (Reimus, *et al.*, 2007). In breccias, porosities are known to be both intercrystalline and intergranular (Keller & Ibrahim, 1982), with preferential flowpaths existing around large, dense clasts. This effect is evident in Figure 3.1(d), where Core 24 is seen to have preferential flowpaths around the relatively large clasts, while Core 19 does not, as the clasts in this sample are generally less than the thickness of sample. Noting the relative size of the clasts of up to 3 cm (illustrated in the CT scan, Figure 3.1(c), Core 24) as compared to the 7.7 mm sample thickness, it is likely that the Core 24 sample thickness studied in the through-diffusion tests is not representative of the connectivity of the pore system over a large scale.



Another likely cause for a reduced effective porosity for the breccia samples tested in this study is anion exclusion. Through-diffusion tests using tritiated water on the same samples would distinguish the contribution of this effect versus the effect of pore connectivity (Van Loon, *et al.*, 2003; Appelo & Wersin, 2007). However, it is noted that this effect is likely relatively small, in comparison to the range of porosities and diffusivities measured between geologic layers and even within a single geologic layer at the study site and the heterogeneities characteristic, in particular, of volcanic breccias (Benning, 2008).

For these experiments, the AA method is insensitive to a change in effective porosity, so that no change in the model is observed with a lower modeled porosity. Mathematically, the explanation for this result is that the porosity essentially only affects the second term on the right hand side of Equation (3.10), which is approximately four orders of magnitude less than the first term of Equation (3.10). Though the AA solution was derived for the transient-state case, it does not appear to be useful for applications where the effective porosity needs to be derived from through-diffusion experiments; this is a significant limitation to this method, as it has been shown that the effective porosity is an essential parameter for modeling the fate and transport of contaminants in fractured rock systems (Löfgren & Neretnieks, 2006).

It has been widely accepted in literature that the use of the time-axis intercept in the TL solution (Equation 3.5) does not provide a reliable estimate of the effective porosity because the intercept is very sensitive to slight changes in the slope of the best-fit line to the experimental data (Grathwohl, 1998; Van Loon, *et al.*, 2003; Appelo & Wersin, 2007; Motellier, *et al.*, 2007). This discrepancy can be seen in Table 3.2, where the effective porosities derived by this method vary substantially from both the bulk porosities and the effective porosities derived by the SA method, generally yielding unlikely estimates. The SA model results indicate more likely estimates of the effective porosities for each sample; furthermore, for each sample, the SA method provides a reduced value of the RSS, indicating the potential for an improved model fit to the experimental data. It is noted that though there is little transient-state data for the PP sample, the best-fit model using the SA yields an effective porosity equal to the measured bulk porosity, which in this case is known fairly accurately through 3-D modeling of CT images. It is noted that due to the well-connected pore structure (shown in Figure 3.13), relatively large pore spaces, and chemical composition of the PP sample, there is no reason to anticipate that the effective porosity of this sample should be less than the bulk porosity. For the TL method, the estimate of the porosity for

the PP sample is substantially improved (18% difference compared to 33% difference) by history-matching using Equation (3.4) versus the use of the time-intercept in Equation (3.5). This history-matching technique using Equation (3.5) did not change the estimated effective porosities for the breccia samples, as compared to that estimated from the time-axis intercept. Due to the demonstrated ability of the SA model to derive a representative estimate of the porosity, the use of the SA model is recommended as an improved method of determining the effective porosity from through-diffusion experiments, when sufficient transient-state data is available.

As noted previously, the derived intrinsic diffusion coefficients from the various methods do not differ substantially from one another, as long as the relevant boundary conditions for the methods are not violated. Since the TL method is the only method that allows direct calculation of the intrinsic diffusion coefficient, this method can be applied to derive a first estimate in order to reduce the number of runs in history-matching techniques for other methods. The subsequent application of the SA method is recommended for the derivation of an effective porosity. Though the use of a sole anionic tracer for this study does not allow distinction of the phenomena that cause the effective porosity to be less than the bulk measured porosity (i.e. unconnected or dead end pores versus anion exclusion or diffuse double layer effects), future studies comparing anion, cation, and tritiated water diffusion could be employed to isolate these influences. However, as has been demonstrated in this study, the analyses of these types of experiments could be dramatically improved by the use of the SA method to derive the effective porosity from transient-state through-diffusion data.

### 3.6 CONCLUSIONS

This study summarized several different solutions to Fick's Law of diffusion and examined their applicability to the analysis of through-diffusion experimental data. The results of the investigations indicated that there is relatively little difference in the intrinsic diffusion coefficient derived using the various through-diffusion solution methods even with a 4% change in the source cell concentration, which is a violation of the boundary conditions for the time-lag and approximate analytical methods. However, for applications in which the effective, or transport, porosity is significantly different from the bulk porosity, the use of a semi-analytical model, such as that developed by Moridis (1998, 1999), is required for the analysis of transient-state through-diffusion experimental data. And thus, in further studies designed to quantify the contributions of the various causes of the differences between the effective porosity and the bulk porosity (i.e.

unconnected pores versus diffuse double layer and/or anion exclusion effects), the application of a solution such as the semi-analytical method is essential, as it provides a substantial improvement to the derivation of effective porosity as compared to the commonly applied time-lag solution.

As was noted in the introduction, not all of the pore spaces in a natural porous medium may be connected and/or available for diffusion. This effect can be seen by comparison of the results of the natural samples, i.e. Core 19 and Core 24, for which the effective porosities are less than the bulk measured porosity, to the results of the porous plate sample, which was manufactured to have a well-connected pore structure. In confirmation of the results of Reimus, *et al.* (2007), this fact may have an important implication on the appropriateness of the scale of the sample measured in through-diffusion experiments. As seen in the Core 24 sample, for example, the derived effective porosity is likely not representative of measurements on a larger scale because the use of a thin slice allows pores to be connected that would otherwise be unconnected at a larger scale.

### 3.7 NOTATION

|          |   |
|----------|---|
| $\alpha$ | Rock capacity factor of the porous medium, dimensionless.   |
| $\delta$ | Constrictivity factor of pore structure, dimensionless.   |
| $\rho_b$ | Bulk dry density of porous medium, g/m <sup>3</sup> .   |
| $\tau$   | Tortuosity of pore structure, dimensionless.  |
| $\phi$   | Porosity of porous medium, dimensionless.   |
| $\phi_e$ | Effective porosity of medium, dimensionless.  |
| $A$      | Cross-sectional area of sample normal to the direction of the diffusional flux, m <sup>2</sup> .  |
| $C$      | Concentration of the diffusing molecule in the pore water, mg/L.  |
| $C_R$    | Concentration of the diffusing molecule in the receiving cell, mg/L.  |
| $C_S$    | Concentration of the diffusing molecule in the source cell, mg/L.   |
| $D_i$    | Intrinsic diffusion coefficient, m <sup>2</sup> /s.   |
| $D_m$    | Molecular, or free water, diffusion coefficient, m <sup>2</sup> /s.   |
| $F_f$    | Formation factor of porous medium, dimensionless.   |
| $J_x$    | One-dimensional diffusional flux of the diffusing molecule per unit area of the porous medium, along the x-axis, mg/(m <sup>2</sup> s). |
| $K_d$    | Sorption coefficient, m <sup>3</sup> /kg.   |
| $L$      | Length of sample in the direction of diffusion, m.  |
| $M_F$    | Mass of diffusing molecule in the sorbed phase, g.  |
| $M_S$    | Mass of diffusing molecule in the source cell, g.   |
| $M_R$    | Mass of diffusing molecule in the receiving cell, g.  |
| $M_W$    | Mass of diffusing molecule in the pore water, g.  |
| $t$      | Time, s.  |
| $V_S$    | Volume of source cell, m <sup>3</sup> .   |
| $V_R$    | Volume of receiving cell, m <sup>3</sup> .  |
| $x$      | Distance, m.  |

### 3.8 ACKNOWLEDGEMENTS

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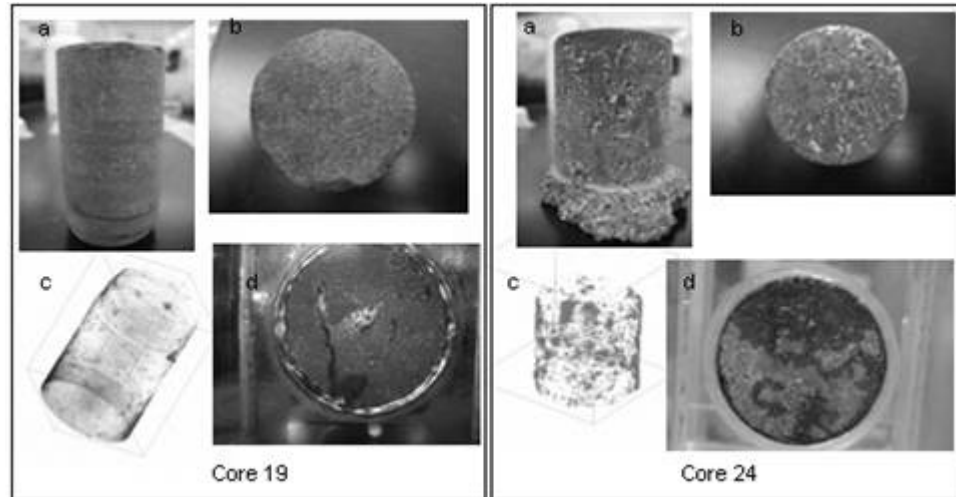
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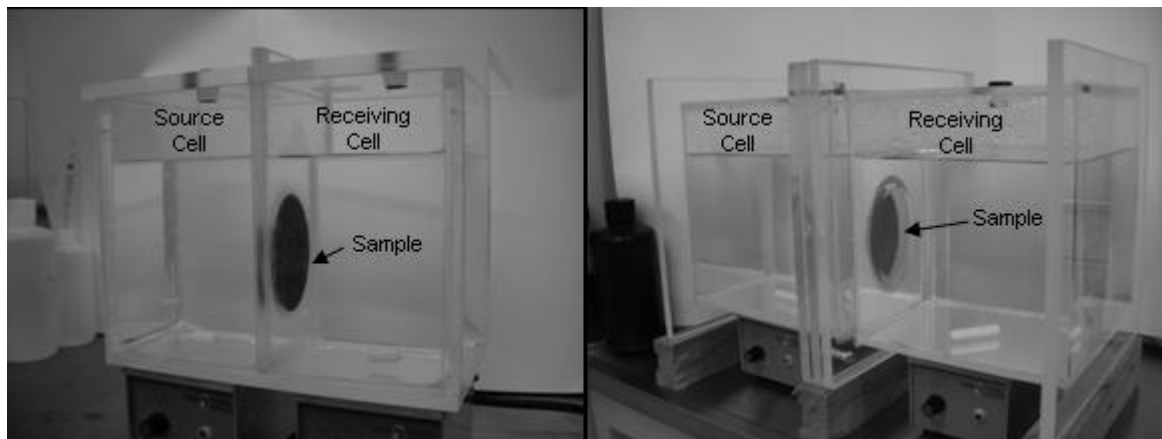
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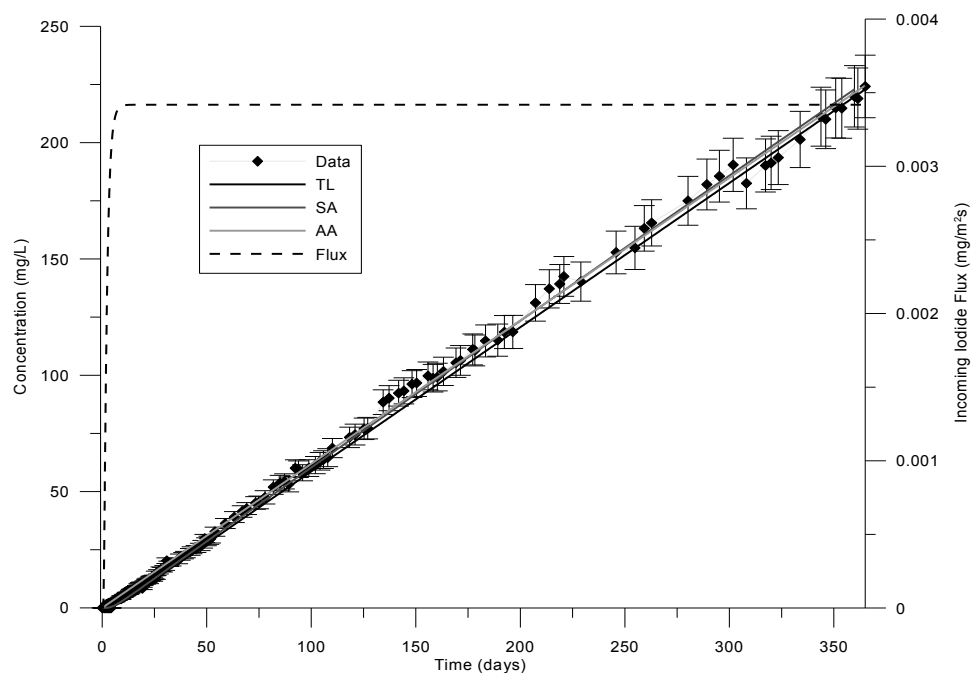




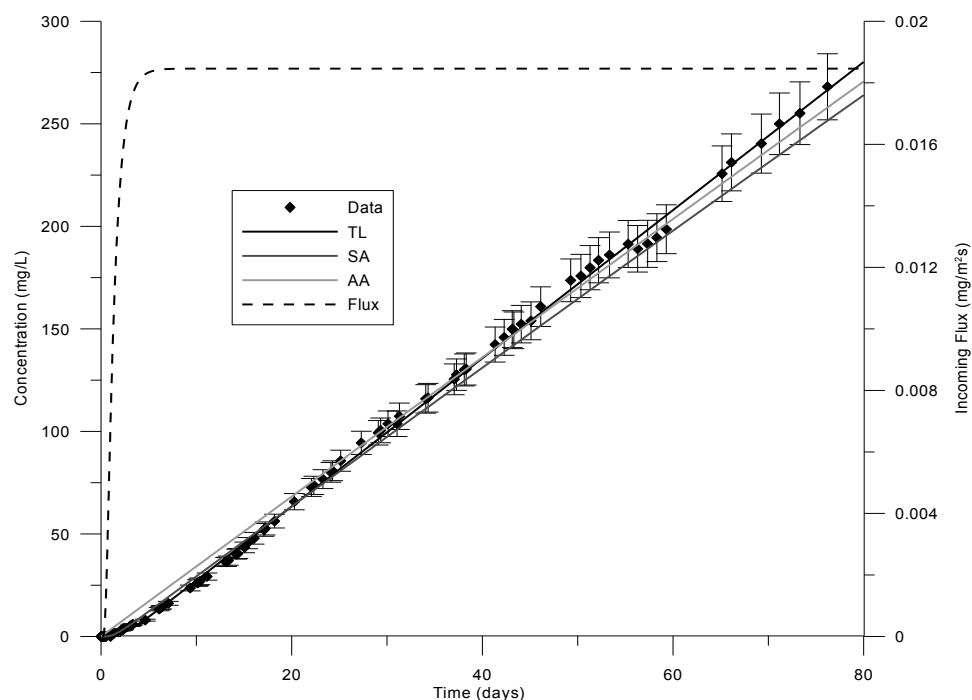
**Figure 3.1 Core 19 and Core 24 breccia samples. (a) (b) Photographs of adjacent core samples, samples are 51 mm in diameter; (c) 3-D view of samples produced by X-ray CT imaging, dark colors represent high densities, 51 mm diameter samples; (d) Photographs of the samples used for the diffusion experiments during the water saturation process, indicating preferential flow paths. The circumference of the samples are darkened by the Lexel® seal. The samples are 89mm in diameter.**



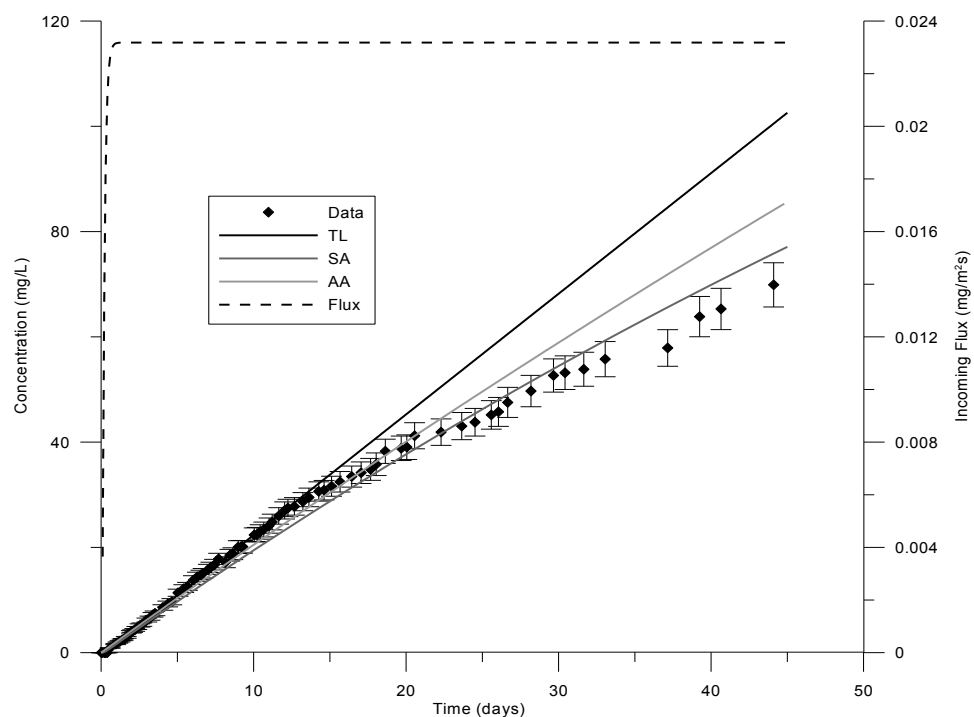
**Figure 3.2 Photographs of the through-diffusion experimental reactors: (a) is used for the Core-19 and Core-24 breccia samples and (b) is used for the manufactured porous plate sample. In 1(b), the sample is affixed to an acrylic center plate, which is clamped between the end plates of the source and receiving cell boxes and sealed with o-rings.**



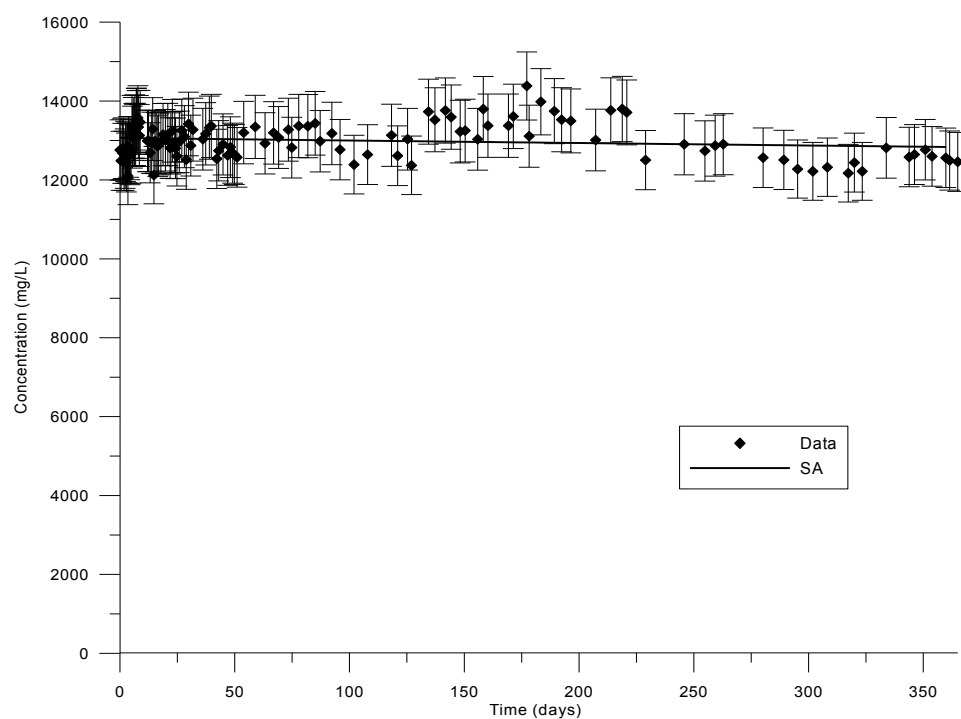
**Figure 3.3** Through-diffusion receiving cell iodide concentration data and time-lag (TL), semi-analytical (SA), and approximate analytical (AA) method solutions for Core 19. The incoming flux indicates the steady-state period.



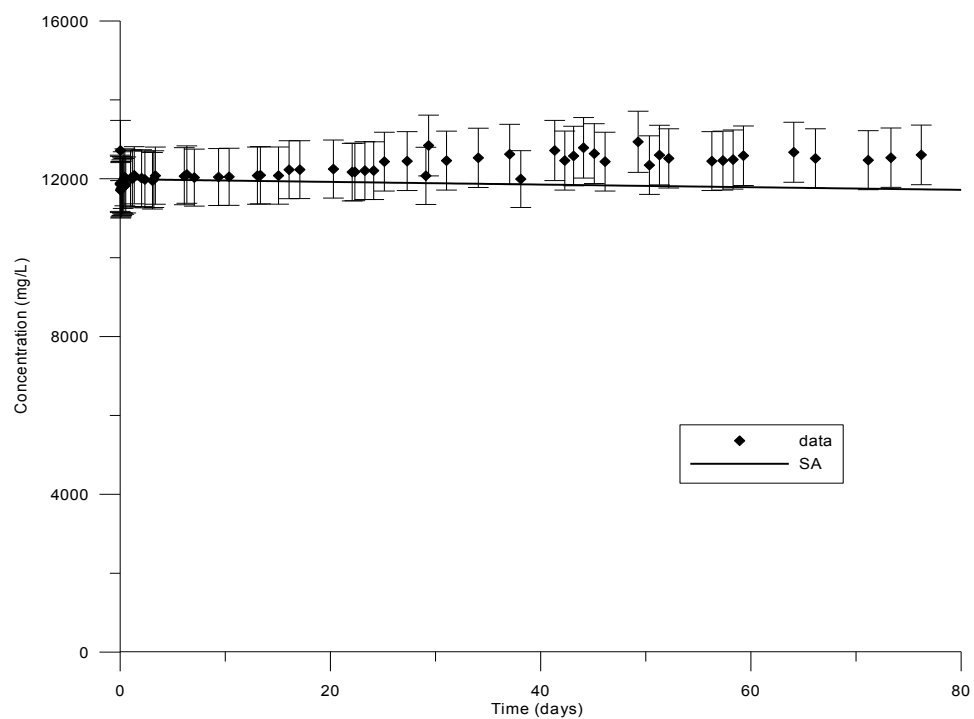
**Figure 3.4** Through-diffusion receiving cell iodide concentration data and time-lag (TL), semi-analytical (SA), and approximate analytical (AA) method solutions for Core 24. The incoming flux indicates the steady-state period.



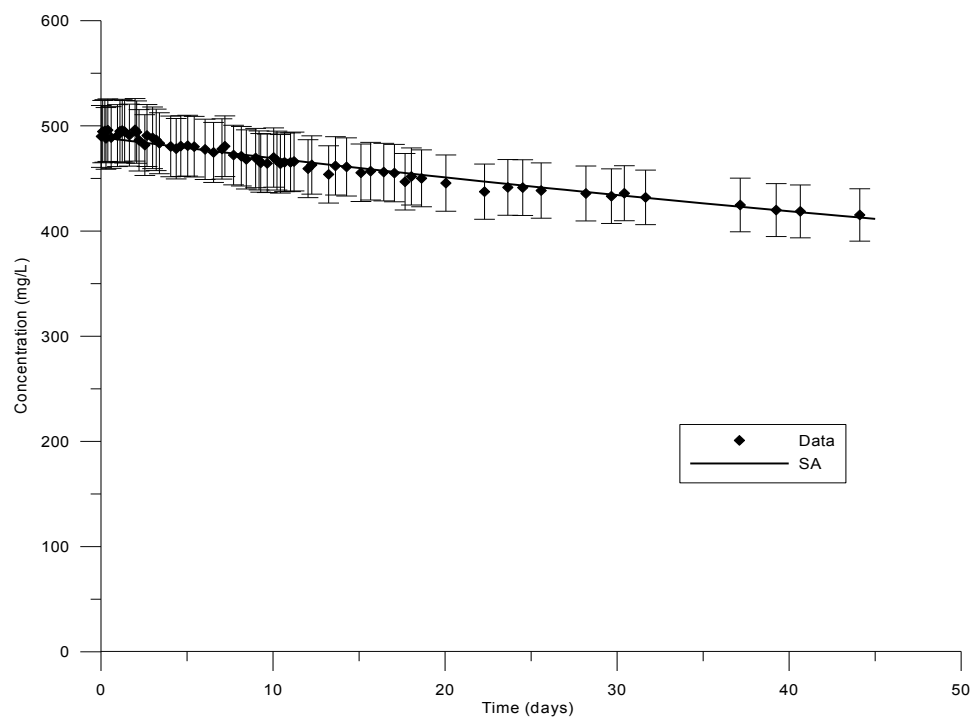
**Figure 3.5** Through-diffusion receiving cell iodide concentration data and time-lag (TL), semi-analytical (SA), and approximate analytical (AA) method solutions for PP. The incoming flux indicates the steady-state period.



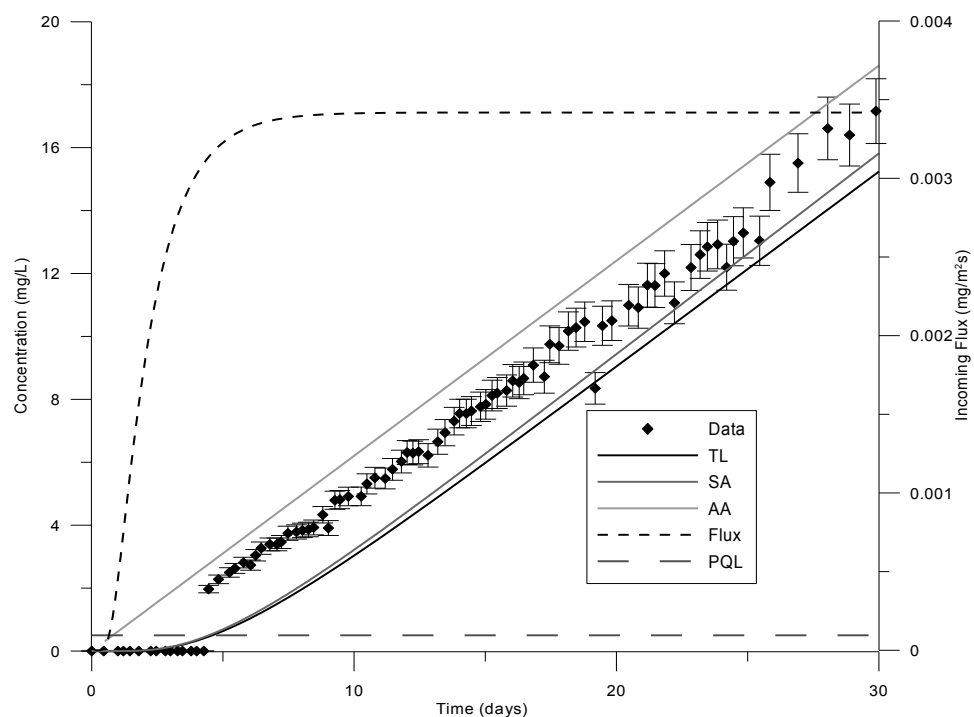
**Figure 3.6** Through-diffusion source cell iodide concentration data and semi-analytical (SA) method solutions for Core 19.



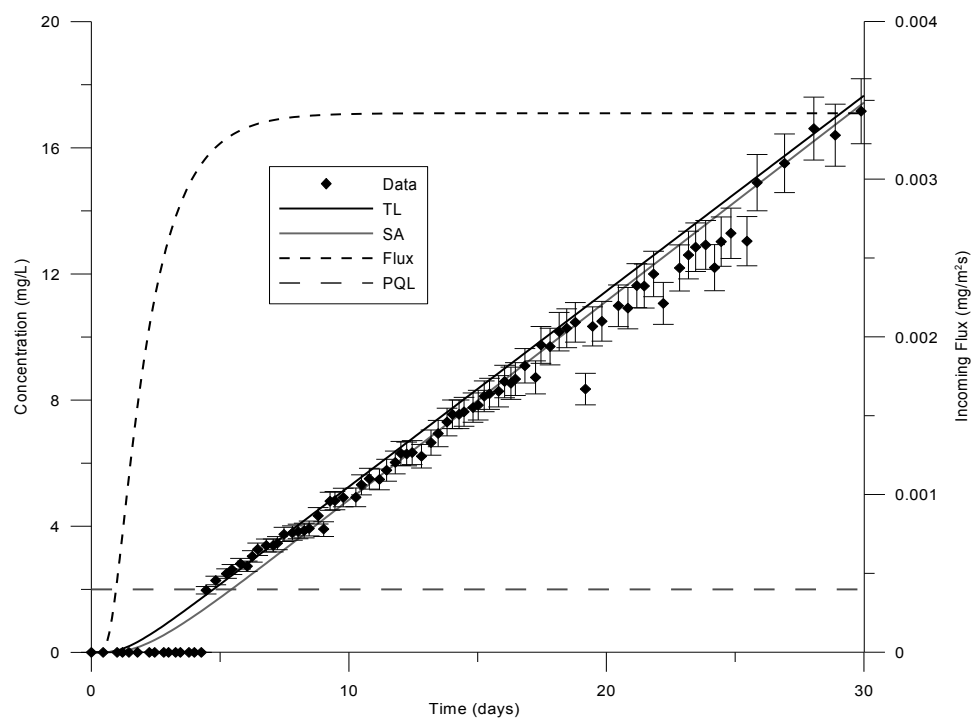
**Figure 3.7 Through-diffusion source cell iodide concentration data and semi-analytical (SA) method solutions for Core 24.**



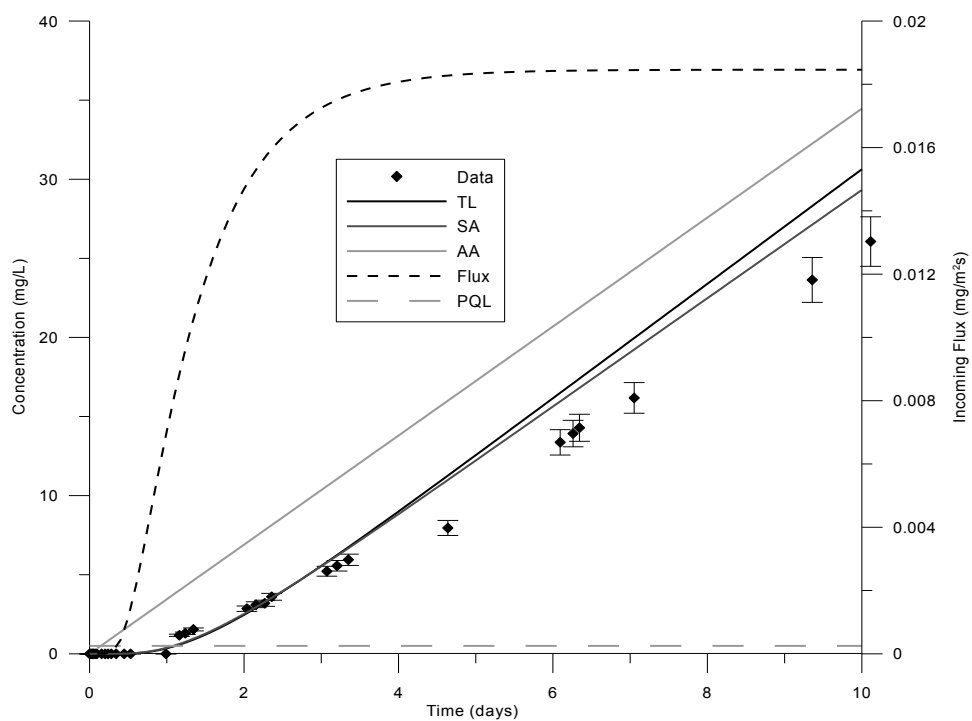
**Figure 3.8 Through-diffusion source cell iodide concentration data and semi-analytical (SA) method solutions for PP.**



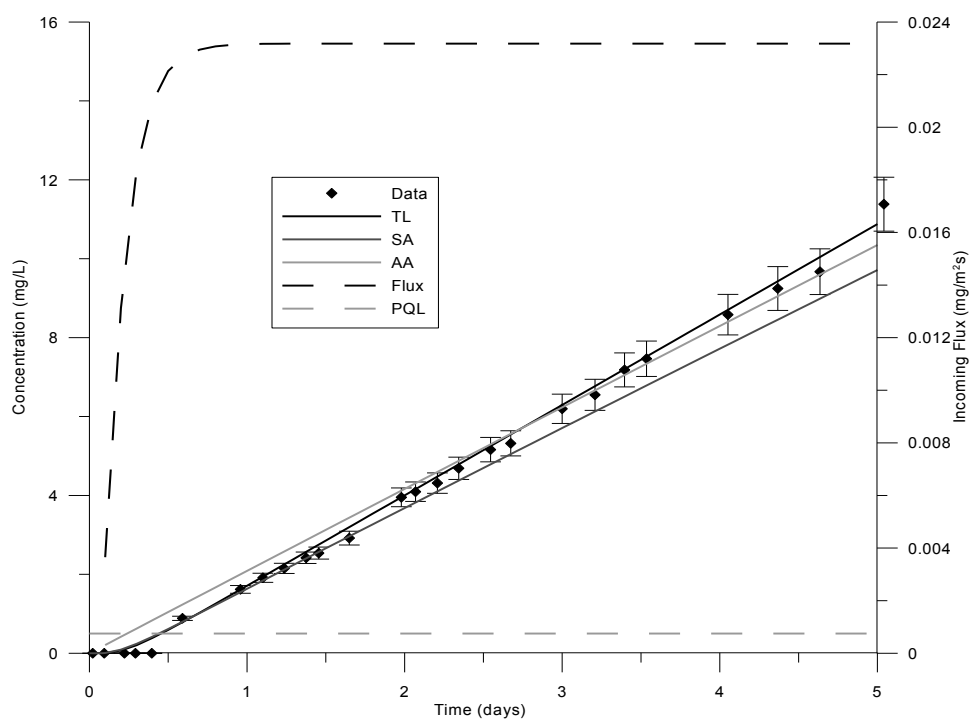
**Figure 3.9** Core 19 transient-state receiving cell iodide concentration data and time-lag (TL), semi-analytical (SA), and approximate analytical (AA) method solutions for bulk porosity. The incoming flux indicates the steady-state period.



**Figure 3.10** Core 19 transient-state receiving cell iodide concentration data and time-lag (TL), semi-analytical (SA), and approximate analytical (AA) method solutions for effective porosity. The incoming flux indicates the steady-state period.



**Figure 3.11** Transient-state receiving cell iodide concentration data and time-lag (TL), semi-analytical (SA), and approximate analytical (AA) method solutions with effective porosity for Core 24. The incoming flux indicates the steady-state period.



**Figure 3.12** Transient-state receiving cell iodide concentration data and time-lag (TL), semi-analytical (SA), and approximate analytical (AA) method solutions with effective porosity for PP. The incoming flux indicates the steady-state period.



**Figure 3.13** A 1 mm x 0.82 mm x 0.28 mm image showing the pore structure of the porous plate sample, produced by X-ray CT technology, scanned at a resolution of 2.24  $\mu\text{m}$ .

**Table 3.1 Summary of the through-diffusion experimental configurations, chemicals, and sample dimensions.**

| Sample            | Bulk Porosity | Sample Diameter (mm) | Sample Thickness (mm) | Initial Source Cell Fluid | Initial Receiving Cell Fluid | Volume Source Cell (L) | Volume Receiving Cell (L) | Experimental Duration (days) |
|-------------------|---------------|----------------------|-----------------------|---------------------------|------------------------------|------------------------|---------------------------|------------------------------|
| Core 19 (Breccia) | 13.7          | 88.9                 | 5.2                   | 0.1 M NaI                 | 0.1 M NaNO <sub>3</sub>      | 2.38                   | 2.40                      | 365                          |
| Core 24 (Breccia) | 16.8          | 88.9                 | 7.7                   | 0.1 M NaI                 | 0.1 M NaNO <sub>3</sub>      | 2.38                   | 2.40                      | 78                           |
| Porous Plate      | 40.9          | 101.6                | 13.0                  | 3.94E-3 M NaI             | 6.95E-3 M NaNO <sub>3</sub>  | 8.10                   | 8.10                      | 45                           |

**Table 3.2 The effective diffusion coefficients, formation factors, and effective porosities derived from the best-fit models to the experimental data for each sample.**

| Sample          | Model     | Intrinsic Diffusion Coefficient for Iodide (m <sup>2</sup> /s) | Formation Factor             | Effective Porosity (%) |
|-----------------|-----------|--|------------------------------|------------------------|
| Core 19 breccia | TL        | $1.32 \pm 0.08 \times 10^{-12}$                                | $7.2 \pm 0.7 \times 10^{-4}$ | $3.9 \pm 0.8$          |
|                 | SA        | $1.36 \pm 0.08 \times 10^{-12}$                                | $7.4 \pm 0.7 \times 10^{-4}$ | $6.0 \pm 0.4$          |
|                 | AA        | $1.32 \pm 0.08 \times 10^{-12}$                                | $7.2 \pm 0.7 \times 10^{-4}$ | -                      |
| Core 24 Breccia | TL        | $1.23 \pm 0.07 \times 10^{-11}$                                | $6.3 \pm 0.6 \times 10^{-3}$ | $26.6 \pm 5.3$         |
|                 | SA        | $1.18 \pm 0.07 \times 10^{-11}$                                | $7.2 \pm 0.6 \times 10^{-3}$ | $15.0 \pm 1.2$         |
|                 | AA        | $1.18 \pm 0.07 \times 10^{-11}$                                | $7.2 \pm 0.6 \times 10^{-3}$ | -                      |
| Manufactured PP | TL (Eq 5) | $6.95 \pm 0.07 \times 10^{-10}$                                | $3.3 \pm 0.4 \times 10^{-1}$ | $54.2 \pm 10.8$        |
|                 | TL (Eq 4) | $6.45 \pm 0.06 \times 10^{-10}$                                | $3.1 \pm 0.4 \times 10^{-1}$ | $33.4 \pm 6.7$         |
|                 | SA        | $6.15 \pm 0.04 \times 10^{-10}$                                | $3.0 \pm 0.2 \times 10^{-1}$ | $41.0 \pm 2.5$         |
|                 | AA        | $6.38 \pm 0.06 \times 10^{-12}$                                | $3.3 \pm 0.4 \times 10^{-1}$ | -                      |



#### **4 THE EFFECTS OF SCALE AND SPATIAL HETEROGENEITIES ON DIFFUSION IN VOLCANIC BRECCIAS AND BASALTS: AMCHITKA ISLAND, ALASKA**

##### **Abstract**

Knowledge of the factors that influence the diffusion of contaminants, such as the diffusivity and the connected porosity, is crucial to modeling the long-term fate and transport of contaminants in subsurface systems with small or negligible advective flow, such as in fractured crystalline rock. Fractured rock is naturally heterogeneous, and hence, understanding the diffusivity (or formation factor) of a molecule through this material becomes a complex problem, with critical concerns about the scale of laboratory measurements and about the spatial variability of these measurements relative to the scale needed for fate and transport modeling. This study employed both electrical and tracer-based laboratory methods to investigate the effects of scale and pore system connectivity on the diffusivity for volcanic matrix rock derived from the study site, a former underground nuclear test site at Amchitka Island, Alaska. The results of these investigations indicate a relatively well-connected pore system with scale effects generally limited approximately 6 cm lengths and well-correlated to observed heterogeneous features. An important conclusion resulting from this study, however, is that there is a potential for the estimated diffusivity to be misrepresented by an order of magnitude if multiple samples or longer sample lengths are not used. Given the relatively large number of measurements resulting from these investigations, an analysis of the probability distribution function (PDF) of the diffusivity, the form of which had previously been unknown, was possible. The PDF of the diffusivity was shown to generally follow a normal distribution for individual geologic layers. However, when all of the geologic layers are considered together, the distribution of the subsurface as a whole was shown to follow a lognormal distribution due to the order of magnitude differences amongst the layers. An understanding of these distributions is essential for future stochastic modeling efforts.

Benning, J.L. and D.L. Barnes. 2008. The effects of scale and spatial heterogeneities on diffusion in volcanic breccias and basalts: Amchitka Island, Alaska. Submitted to *Journal of Contaminant Hydrology*.

## 4.1 INTRODUCTION

When the advective flow in the subsurface is small or negligible, the diffusion of contaminants can play a dominant role in their transport. This is often the case when the subsurface is comprised of fractured crystalline rock (Neretnieks, 1980, 1993). Several comprehensive studies on diffusive transport have been conducted in this geologic material owing to the choice of this media for nuclear waste repositories and as the host media for several historic underground nuclear tests (Bradbury and Green, 1985; Skagius and Neretnieks, 1986a; Reimus, *et al.*, 2007). Others have established that the knowledge of the factors that influence the diffusion of contaminants, such as the diffusivity (or formation factor, the ratio of the intrinsic diffusion coefficient to the molecular diffusion coefficient) and the connected (or effective) porosity, is crucial to modeling the long-term fate and transport of contaminants in these systems (Bradbury and Green, 1985; Skagius and Neretnieks, 1986a; Löfgren & Neretnieks, 2006; Appelo and Wersin, 2007). However, accurate measurement of these factors, primarily formation factor, is difficult due to the spatial heterogeneity of these properties and the possible scale dependency of these measurements.

The objectives of this study were to investigate the effects of scale and pore system connectivity on the intrinsic diffusion coefficient for volcanic matrix rock and to investigate the impacts of spatial heterogeneities, particularly in regards to highly heterogeneous breccias, on intrinsic diffusion coefficients. For the study site, Amchitka Island, a former underground nuclear test site, previous groundwater transport models have indicated that the porosity and the intrinsic diffusion coefficient are two of the key uncertainties (Hassan, *et al.*, 2002). Thus, an associated objective of this study was to assess the range of diffusivities found in the different rock types that comprise the subsurface of the island. Recommendations for radionuclide transport modeling at Amchitka Island are made in light of these effects.

## 4.2 BACKGROUND

### 4.2.1 *The effects of scale on diffusion*

Fractured rock is naturally heterogeneous, and hence, understanding the diffusivity of a molecule through this material becomes a complex problem, with critical concerns about the scale of laboratory measurements relative to the field scale and about the spatial variability of these measurements relative to the scale needed for fate and transport modeling. Numerous studies

have indicated the influence of scale on such parameters as porosity (Bear, 1972) and longitudinal dispersivity (Gelhar, *et al.*, 1992), and it logically follows that there may be similar effects of scale on diffusion, particularly in fractured rock. The potential impacts of this inference are particularly a concern with diffusion in fractured rock, as the properties of the media can be very heterogeneous over small scales. Additionally, because the diffusion process is inherently very slow, small samples are typically chosen for laboratory studies, making it difficult to represent the degree of heterogeneity present in the rock. Lever, *et al.* (1985) suggested a minimum thickness for through-diffusion studies on granites of 5 mm due to the interconnectivity of pores at lesser thicknesses that would otherwise be unconnected at greater lengths. However, this minimum thickness depends on the nature of the rock, and one would anticipate that it may be different for different materials.

Atkinson and Titchell (1985) and Skagius (1986) investigated the effects of scale on laboratory-scale diffusion measurements via electrical resistivity methods. Atkinson and Titchell compared the derived formation factors for an Altnabreac granite sample and a Cornish granite sample at decreasing sample lengths, down to 1 cm. The results indicate that the Altnabreac granite, which is characterized by smaller microstructural scale than the Cornish granite, displayed an increase of a factor of 2 in the formation factor at lengths below 5 cm, with no additional changes from 5 cm to 25 cm. However, in the Cornish granite, there was considerably greater scatter in the measured formation factor as a function of diffusion length, presumably due to the greater heterogeneity of that rock. Skagius found that for Swedish crystalline rocks, the conductivity at 5 cm was approximately half the conductivity at 1 cm, with no further scale effects observed between 5 cm and 30 cm.

Valkiainen, *et al.* (1996) studied the effects of sample length on the derived intrinsic diffusion coefficients (as defined by Bradbury and Green, 1985) from through-diffusion experiments on samples of 2, 4, and 6 cm thicknesses. For the Finnish granites studied, their results indicated that, though there was some decrease in pore connectivity and diffusion coefficients between 2 and 4 cm, this decrease was minimal. Löfgren and Neretnieks (2006) investigated the effects of the sample length on the diffusivity for granites and mafic vulcanites using through-diffusion tests, electrical resistivity (AC and DC) experiments, and through-electromigration (TEM) tests. Their results indicated that there were no discernable effects of scale, as the variability between

samples was greater than any effects of scale, thus indicating that for the studied rocks, the pore system was well-connected.

#### 4.2.2 *The effects of spatial heterogeneities on diffusion*

Numerous studies have been conducted to assess the spatial heterogeneity of the diffusion of molecules through fractured rock. These studies have focused on various scales of investigations, from inter-site comparisons (Reimus, *et al.*, 2007), to comparisons across a site (Bradbury and Green, 1985; Skagius and Neretnieks, 1986a, 1986b; Yamaguchi and Nakayama, 1998), and to studies into the effects of microscopic heterogeneities (Siitari-Kauppi, *et al.*, 1997; Tidwell, *et al.*, 2000; Altman, *et al.*, 2004). In all of these studies, the authors concluded that the spatial variability of diffusion properties is strongly tied to the rock's porosity, and possibly more importantly, to variations in the degree of connectivity of the pore system. As noted by Löfgren and Neretnieks (2006), numerous worldwide studies on intrusive igneous rocks have reported that the intrinsic diffusion coefficients are in the range of  $10^{-15}$  to  $10^{-12}$  m<sup>2</sup>/s. Reimus, *et al.* (2007) report a range of  $10^{-12}$  to  $10^{-10}$  for volcanic rocks. These authors indicated that the diffusivity of rocks was well-correlated with both the porosity and the permeability.

On the laboratory scale, the influences of heterogeneous porosity on diffusion coefficients have been investigated by Siitari-Kauppi, *et al.* (1997), Tidwell, *et al.* (2000), and Altman, *et al.*, 2004. Siitari-Kauppi, *et al.* (1997) examined heterogeneities of mica gneiss samples and tonalite samples with varying degrees of alteration and found that the mica gneiss samples displayed a dominance of intracrystalline porosity, and the bulk porosities and diffusivities were lower than in the unaltered tonalite samples, which displayed a dominance of intercrystalline porosity. Tidwell, *et al.* (2000) and Altman, *et al.* (2004) used X-ray absorption imaging to examine the relationship between heterogeneities in porosity and diffusion at the sub-millimeter scale in Culebra dolomite samples from New Mexico and fractured granodiorite samples from Japan, respectively. In both studies, spatial variabilities in diffusion coefficients were well-correlated with heterogeneities in void space features.

It has been demonstrated that the degree of connectivity of the pore structure plays an important role in the movement of molecules by diffusion in fractured rock, though different investigations have lead to different conclusions (Löfgren and Neretnieks, 2006). Schild, *et al.* (2001) conducted *in situ* testing of connected porosity in granitic matrix rocks with porosities less than

1% using acrylic impregnation methods. Their study found that the rocks displayed a well-connected system of microcracks, but that typical laboratory methods of measuring porosity tended to overestimate the porosity. These results were somewhat in contradiction of an earlier, more qualitative study by Heath, *et al.* (1992). This study investigated spatial variability of diffusion by examining changes in microstructure, physical properties, and geochemical properties of rock at increasing distances from fractures in samples representing El Berrocal granites in Spain, Stripa granite in Sweden, and Whiteshell granite in Canada. The study's results indicated that all of the samples display a "zone of enhanced mobility" surrounding the fracture, which extends from between 25 mm to 80 mm, depending on the rock type and degree of alteration. The authors concluded that in undisturbed rock, not all of the media may be available for retardation via diffusion, as many models assume. Later investigations into the connectivity of the pore system in Swedish granites by Löfgren and Neretnieks (2006) concluded that the pore systems were well-connected at a scale of meters. It is noted, however, that all of these studies focused on the connectivity of intrusive igneous rocks, and that for other types of matrix rocks, the conclusions could be different.

#### 4.2.3 *Amchitka Island*

Amchitka Island is one of the western Aleutian Islands and is part of a group of islands known as the Rat Islands (Figure 4.1). Three underground nuclear tests were conducted on Amchitka between 1965 and 1971. The first test, Long Shot, was an 80-kt nuclear explosion detonated on 29 October 1965 at a depth of 701 m (2300 ft) below ground surface. The 1-Mt nuclear device, named Milrow, was detonated on 2 October 1969 at a depth of 1218 m (3996 ft) below ground surface. The final explosion, Cannikin, at 5-Mt, was the largest nuclear device ever detonated in the US testing program and was detonated on 6 November 1971 at a depth of 1792 m (5843 ft) (Merritt and Fuller, 1977; US Congress, 1989).

As part of a process undertaken by the U.S. Department of Energy to assess the human health risk resulting from the possible release of radionuclides to the marine environment as a consequence of the tests, Hassan, *et al.* (2002) produced a model to describe Amchitka Island's groundwater flow and the transport of radionuclides released during the three tests. This modeling effort also included sensitivity analyses in order to ascertain the relative significance of the many uncertainties in the model. The analyses revealed that two of the key uncertainties are the porosity and the intrinsic diffusion coefficient, indicating the importance of accurately

representing the intrinsic diffusion in fractured rock contaminant transport modeling. Later groundwater and transport models for the island, summarized in Benning, *et al.* (2008), based on additional data reduced some of the uncertainties associated with the island's earlier models; however, as noted by Pletnikoff (2008) and Benning, *et al.* (2008), there are still remaining concerns regarding the uncertainties, namely the porosity and retardation through diffusion, associated with the modeling efforts at the site.

The intrinsic diffusion coefficients at Amchitka Island have been investigated in basalts and breccias by Brown (2000) and in an andesite sample by Raghupatruni (2004). Brown found intrinsic diffusion coefficients from small samples (with maximum sizes of 3.8 x 1.9 x 1.9 cm and 2 x 2 x 0.5 cm) of  $5.9 \times 10^{-11}$  and  $6.8 \times 10^{-10}$  m<sup>2</sup>/s for basalt samples and  $1.2 \times 10^{-11}$  and  $2.6 \times 10^{-11}$  m<sup>2</sup>/s for the breccia samples. Regarding duplicate experiments in that study, it was noted that the variability of the breccia diffusion coefficients was greater than for the basalt, and this is likely due to the more heterogeneous nature of breccia, particularly at the scale of the samples used. The origin of the core samples used in this study was given as in the vicinity of the Cannikin test shot, though no information was given as to the depth from which the samples were obtained. Raghupatruni (2004) found intrinsic diffusion coefficients of  $4 \times 10^{-11}$  and  $1.3 \times 10^{-9}$  from adjacent samples of andesite core, originating from a core in the vicinity of the Milrow test shot, with no information given on the depth from which the sample was obtained. The higher value is in the same order of magnitude as the molecular diffusion coefficient, indicating the likelihood that a microporous preferential pathway existed in the sample. The order of magnitude differences between the two andesite samples and the two-order of magnitude differences between the andesite diffusivities and those of the basalts and breccias indicate that the spatial variability of diffusivities at the island warranted further investigations.

## 4.3 THEORY

### 4.3.1 Through-diffusion experiments

In a typical through-diffusion experiment, several parameters, including the intrinsic diffusion coefficient, the formation factor, and the effective porosity, are derived from the application of Fick's Law of diffusion to the experimental data. In the ensuing discussion, it is important to clarify the definitions of these parameters, since they are defined differently by many researchers. In this study, the intrinsic diffusion coefficient,  $D_i$ , is defined as (Van Brakel and Heertjes, 1974):

$$D_i = D_m \left( \frac{\phi_e \delta}{\tau^2} \right) = D_m F_f \quad (4.1)$$

where  $D_m$  is the free water or molecular diffusion coefficient,  $\phi_e$  is the effective or transport porosity,  $\delta$  is the constrictivity, and  $\tau$  is the tortuosity of the porous medium.  $F_f$  is the formation factor and is considered to be solely a property of the porous medium and not a property of diffusing molecule; however, as noted by Snyder (2001), it can reflect the specific conditions of the experiment.

There are numerous solutions for Fick's Law of diffusion to determine the intrinsic diffusion coefficient and effective porosity from through-diffusion experimental data. Some of these solutions and their assumed boundary conditions are summarized and compared in Benning and Barnes (2008). The two methods employed in these investigations are the time-lag method (Crank, 1975; Bradbury and Green, 1985; Skagius and Neretnieks, 1986a) and the semi-analytical method (Moridis, 1998 and 1999). For typical through-diffusion experiments conducted on relatively thin core samples, the semi-analytical method was used to derive the intrinsic diffusion coefficients and effective porosities. The semi-analytical solution provides a more reliable estimate of the effective porosity than the time-lag solution when there is sufficient transient-state data for analysis (Benning and Barnes, 2008).

As indicated in Equation (4.1), the formation factor for each sample is calculated by dividing the intrinsic diffusion coefficient by the molecular diffusion coefficient for iodide. The molecular diffusion coefficient of iodide at 25°C is  $2.048 \times 10^{-9} \text{ m}^2/\text{s}$  at 25°C (CRC, 2008). This value was adjusted for the correct temperature for each experiment using the Wilke and Change Equation (Treybal, 1980) with published parameters (CRC, 2008). In the experiments, the receiving cell contained an electrolyte solution at 1 M concentration, which could introduce some error due to counter-diffusion and electrochemical effects. However, studies by Stokes, *et al.* (1957), Cussler (1984), Daniel and Albright (1991), and Snyder (2001) indicate that at the molarities used in these experiments, the decrease in the molecular diffusion coefficient is less than 10%.

#### 4.3.2 Electrical conductivity experiments

Electrical conductivity testing has commonly been applied to measure formation factors in rock samples (Keller and Ibrahim, 1982; Atkinson & Titchell, 1985; Skagius & Neretnieks, 1986b;

Snyder, 2001; Löfgren and Neretnieks, 2006; Mayr, *et al.*, 2007). In this method, core samples are saturated with an electrolyte solution at concentrations high enough to overcome potential surface conductivity effects, and then conductivity of the saturated core is measured (Brace, *et al.*, 1965; Skagius & Neretnieks, 1986b; Snyder, 2001). Conductance of the saturated sample will be caused almost exclusively by the solution filling the pore spaces if the rock minerals are nonconducting, and thus depends on the same factors as does the effective diffusion. Klinkenberg (1951) relates the ratio of  $D_e$  to molecular diffusion ( $D_m$ ) to the ratio of the conductance of the solution-saturated rock ( $\sigma_R$ ) to the conductance of the salt solution ( $\sigma_s$ ):

$$F_f = \left( \frac{D_e}{D_m} \right) = \left( \frac{\sigma_R}{\sigma_s} \right) \quad (4.2)$$

where the conductivity of the brine-saturated rock is determined by measuring the potential drop (V) across electrodes and is calculated the relationship:

$$\sigma_R = \frac{iL}{VA} \quad (4.3)$$

where  $i$  is the current,  $L$  is the length of the section of rock across which the voltage is being measured, and  $A$  is the cross-sectional area of the rock.

#### 4.4 MATERIALS AND METHODS

##### 4.4.1 Samples

The investigations focused on core samples from Amchitka Island, Alaska, at the UAe-1 drill hole, which is in the immediate vicinity of the Cannikin underground nuclear test shot. The drill hole was advanced in 1965 as an exploratory core prior to the nuclear detonations. Samples for the diffusion investigations are limited to the remaining core samples that are still intact due to the high costs and health risks associated with obtaining post testing core samples from Amchitka Island. A list of the samples tested in these studies, including the lithologic descriptions and sample depths, is included in Table 4.1. For Cores 7, 8, and 24, multiple samples were tested from the same lithologic layer; these adjacent samples are denoted as #1, #2, etc., throughout this paper. Preliminary electrical conductivity investigations were conducted on two samples, an andesite derived from the UAe-2 drill hole, in the immediate vicinity of the Milrow test shot, and



a porous breccia (Core 87) derived from the UA-1 drill hole, in the Cannikin test shot vicinity. Due to weathering of the core sample boxes, the sample depth from the UAe-2 core sample was not identifiable. However the results of the two samples are included because they represent the highest and lowest estimated rock diffusivities at the site. All of the core samples investigated were 89 mm (3.5 inches) in diameter. Prior to conducting other investigations, the bulk porosity of each sample was measured via the water saturation method (Fetter, 1994), in which all samples were oven-dried until a stable mass was achieved and then saturated under vacuum pressure. The densities of the saturating fluid, discussed in the following, were measured and applied to the porosity calculation.

#### 4.4.2 *Experimental*

##### 4.4.2.1 Through-diffusion

The through-diffusion (TD) experiments using iodide as a conservative tracer were conducted as described in literature (Bradbury and Green, 1985; Skagius and Neretnieks, 1986a; Snyder, 2001) on two breccia samples derived from Cores 19 and 24. The Core 19 and Core 24 samples were cut using a diamond saw to thicknesses of 5.2 mm and 7.7 mm, respectively. The dry samples were affixed to an acrylic plate using Lexel® caulk. The plate was then affixed into an acrylic box, shown in Figure 4.2a. The receiving cell was filled with 0.1 M sodium nitrate ( $\text{NaNO}_3$ ) and allowed ample time to achieve rock saturation, based on conservative estimates using the measured permeability of each sample. The source cell was then filled with a conservative tracer solution, 0.1 M sodium iodide ( $\text{NaI}$ ), with the solution volume adjusted to achieve equal hydrostatic pressures on either side of the rock sample. Throughout the experimental duration, 5 mL samples were collected from both the source and receiving cells, and after the sample event, 5 mL of 0.1 M  $\text{NaI}$  and 0.1 M  $\text{NaNO}_3$  were replaced in the source and receiving cells, respectively. The experiments were conducted at constant temperatures of  $21 \pm 1^\circ\text{C}$  and  $23 \pm 0.5^\circ\text{C}$  for the Core 19 and Core 24 experiments, respectively. Each cell was kept mixed throughout the experimental duration through the use of magnetic stir bars. The experimental design and uncertainty analyses are discussed in more thorough detail in Benning and Barnes (2008).

##### 4.4.2.2 Modified through-diffusion

The typical through-diffusion experimental apparatus is generally limited to thin slices of rock. To examine the potential effects of scale, a modified through-diffusion experimental reactor was

designed to accommodate samples thicker than the size of the clasts present in the breccia samples. These modified through-diffusion (MTD) tests were conducted on 48.5 mm and 55.9 mm slices cut from the Core 19 and Core 24 breccia samples, respectively. In preparation for the tests, the samples were first washed in deionized water and then oven-dried. The samples were then placed in a fabricated mold and coated around the circumference via injection of Flexane® polyurethane. The two ends were left uncoated so that diffusion of a tracer can occur only along the axial direction. The molded coating includes a ridge which acts as an O-ring to seal the two ends of the diffusion reactor. The aluminum reactor cells (see Figure 4.2c), with the coated rock in between are compressed and bolted together, with the rock dividing the source and measurement cells. The receiving cell was filled with a 0.1 M  $\text{NaNO}_3$  solution, connected with tubing to a secondary receiving solution reservoir. The rock sample was saturated with this solution under vacuum pressure.

Once saturation had been achieved, the source cell was filled with a 0.1 M  $\text{NaI}$  tracer solution. Both the source cell and receiving cells were connected to secondary reservoirs, such that the total cell volumes were approximately 18 L and 2.4 L for the source and receiving cells, respectively. The use of the secondary reservoirs enabled mechanical mixing so that samples would be representative of the entire cell volumes. For the source cells, the use of a large volume secondary reservoir was used to approximate a constant and relatively high source cell concentration condition in comparison to the receiving cell concentration. Both the source and receiving cells were kept mixed by circulating fluid at low flows using submersible pumps in the respective source and receiving cell secondary reservoirs. The pumps were set on timers in order to minimize heating. The experiments were conducted at constant temperatures of  $23 \pm 0.5^\circ\text{C}$ .

The Core 19 sample reactor leaked after approximately 2.2 years, prior to reaching steady-state conditions, and the results of this experiment were not sufficient to allow the determination of a diffusion coefficient. The Core 24 sample reactor source pump failed after approximately 1 year, causing a change in the early-time boundary conditions for the experiment. After a new pump was installed, steady-state conditions were achieved, allowing the use of the time-lag solution to determine the intrinsic diffusion coefficient of this sample. The source cell concentration was constant, within experimental error, during this time period. This equipment failure prohibited the use of the semi-analytical solution to Fick's Law and the intrinsic diffusion coefficient had to

be calculated using the time-lag solution. The lack of transient-state data prevented the determination of the effective porosity for this sample.

#### 4.4.2.3 Chemical analyses

Iodide concentrations were measured by ion chromatography, using a Dionex AS40 Autosampler with an AS-11 Analytical Column and an AG-11 Guard Column and sodium bicarbonate as an eluent. The analytical error was assessed to be a maximum of 6%, and the method detection limit was 2 mg/L for all but the Core 24 TD test, which had a detection limit of 0.5 mg/L as a result of analytical method modifications. The analytical methods, instrument and measurement errors, and uncertainty analyses are discussed in detail in Benning and Barnes (2008).

#### 4.4.2.4 Electrical resistivity

Core samples were oven-dried, then saturated with a 1 M sodium chloride (NaCl) solution under vacuum pressures over a period of four weeks to six months, depending on the size and porosity of the sample. Once saturated, the cores were wrapped in a test sleeve. The test sleeve was constructed of neoprene, with a series of electrodes (rings of copper wire) affixed at 1 cm separations (except for the Core 24 #1 sample test, which used 2 cm separations) equidistantly along the length of the sleeve (along the axial direction on the corresponding core sample). Copper plate electrodes were attached to each end of the core and a conductive gel was used between the rock and plate to ensure contact. A direct current was passed through the sample with a system potential of 3 V and a system current of approximately 1 mA. The experimental system is illustrated in Figure 4.2b. Preliminary electrical conductivity tests were conducted without the use of the series of copper wire rings, according to the methods described in Telford (1990), on the UAe-2 andesite and Core 87 breccia samples.

The electrical potential across pairs of adjacent electrodes was measured across the length of the rock sample in order to estimate the effects of spatial heterogeneities on diffusion coefficients. For investigations into the effects of scale, the electrical potential was measured across pairs of electrodes spaced at increasing length intervals (i.e. from a 1 cm length, to 2 cm length, etc.). Since the current across the circuit changed with time, it was simultaneously measured and recorded with the potential readings for use in Equation (4.3); the maximum decrease in the current for the experiments was 13%, but typically was less than 5%. The brine solution

conductivity was measured for each experiment using a standard conductivity probe and meter, and this measurement was applied in Equation (4.2) to determine the sample formation factor.

Though no formal uncertainty analysis was performed on these experiments, one of the major issues with the experimental method results from the use of DC. The use of DC in these tests can result in the accumulation of charge on the electrodes (Löfgren and Neretnieks, 2006). A series of tests were conducted to determine the effects of the use of DC on the results. In the first test (on the Core 24 #1 breccia sample), a 12 V power source was used for the system, with a system current of approximately 0.02 A. In these tests, the effect of charge accumulation was evident. Based on this, all subsequent experiments were performed using a system potential of 3 V, with a system current of approximately 1 mA to minimize these effects. Charge accumulation was not evident under these conditions. As a secondary check, a conventional resistivity sounding meter (OYO Co., Ltd., McOHM model-2115) was used on the same core sample. The meter alternates direct current with a square wave function at a frequency of a few hertz to eliminate charge accumulation of electrodes. The results from this test were within 30% of the results obtained with DC current with relatively low voltage and current. As a tertiary check to the potential influences of charge accumulation, the experiments were all immediately repeated and several of the experiments were repeated with the system polarity reversed. The experimental error from repeat experiments and reverse polarity experiments were a maximum of 12% and 9%, respectively, though generally, the errors were less than 5% in both cases. Löfgren and Neretnieks (2006) performed comparisons of formation factors derived from AC methods and DC methods. In their experiments, the authors eliminated the effects of charge accumulation in the DC methods through the use of a secondary electrolyte reservoir on both the cathode and anode sides of the circuit. The differences between the formation factors derived by the AC and DC methods in that study were approximately 10% at maximum.

## 4.5 RESULTS AND DISCUSSION

### 4.5.1 *The effects of scale on diffusion*

The through-diffusion experimental results and the subsequent derivation of the intrinsic diffusion coefficients and effective porosities are presented in Benning and Barnes (2008). The uncertainty analyses associated with these methods are also discussed in Benning and Barnes

(2008). The analysis of experimental data and the associated uncertainty analysis for the modified through-diffusion experiment were performed according to the same methods.

To examine the potential effects of scale, or pore connectivity, the intrinsic diffusion coefficients, measured bulk porosities, effective porosities (where applicable), and formation factors for the Core 19 and Core 24 samples are summarized in Table 4.2, along with the associated sample length and method of measurement for each value.

The formation factor derived through the electrical conductivity testing for the Core 19 sample is a factor of 1.6 to 5.0 greater than the formation factor derived by the through-diffusion experiment. This discrepancy is consistent with the results of others, such as Ohlsson (2000) and Löfgren and Neretnieks (2006), who found that formation factors derived by electrical methods were higher than those derived from tracer based methods by approximately a factor of 2 for the Swedish granites studied. Walter (1982) reported similar results for volcanic tuff samples. Several authors propose that the conductivity of the rock minerals and anion exclusion in the tracer-based methods are potential causes for these differences (Keller and Ibrahim, 1982; Löfgren & Neretnieks, 2006).

The formation factor of the first Core 24 sample tested using electrical methods is a factor of 1.4 to 1.9 greater than that derived by the through-diffusion experiment and a factor of 2.1 to 2.7 greater than that derived by the modified through-diffusion experiment (Table 4.2). However, the measured porosity of that sample (Core 24 #1), 19.0%, is greater than the measured porosities, 16.3 to 16.8%, of the samples tested with the through-diffusion and modified through-diffusion methods. In comparison, the formation factors derived by the through-diffusion and modified through-diffusion methods both fall within the range of those estimated by electrical methods on a similar porosity sample (Core 24 #2), indicating that either the mineral content of this sample is not influencing the formation factor derived by electrical methods or that anion exclusion in the tracer methods is negligible.

The formation factors derived from increasing sample axial lengths in the electrical conductivity experiments for all of the samples indicated in Table 4.1 are illustrated as a function of experimental length in Figure 4.3. Fourteen samples were tested from nine different core locations. In most of the samples, there is some variability in formation factor with increasing sample length, but then at some length, the formation factor approaches an approximately

asymptotic value, indicating no additional scale dependency. This length is different for each sample and, as will be discussed in the subsequent, depends on the degree of heterogeneity in the sample. The approximate asymptotic formation factor value, chosen as less than  $\pm 10\%$  variation, and the approximate length required to achieve that value for each sample are summarized in Table 4.3. In most of the samples, the effect of scale, or the length required to achieve a constant is limited to less than 7 cm; and for 8 of the 14 samples, this length is less than 5 cm. This result is comparable to the observations on granites by others (Atkinson and Titchell, 1985; Skagius, 1986; Valkiainen, *et al.*, 1996). However, two samples, Core 4 and Core 7 #1, exhibited greater effects of scale in the formation factors, with the lengths of 15 cm and 20 cm, respectively, required to achieve an approximately constant value; though the appearance of this effect in Figure 4.3 is somewhat deceptive due to the scaling employed in that figure. The Core 4 basalt sample contained an unweathered, axial fracture in the central portion of the sample that yielded higher formation factor values in that portion. The Core 7 #1 breccia sample contained a large, dense 7.5-cm clast containing phenocrysts and open vesicles, which likely contributed to the greater scale effect exhibited in this sample. The specific influence of this clast is difficult to ascertain; it is comprised of a low porosity matrix material that would inhibit the diffusive transport of molecules, however, preferential flow surrounding such clasts in the breccia samples is also suspected (Keller and Ibrahim, 1982; Benning and Barnes, 2008).

#### 4.5.2 *The effects of spatial heterogeneities on diffusion*

The resulting maximum, minimum, and average formation factors derived through electrical conductivity testing of adjacent 1 cm (2 cm sections for the 24-cm long Core 24 sample) are summarized for each sample tested in Table 4.3. The “factor” difference indicates the ratio of the maximum to minimum estimated formation factor for each sample and indicates the proportional variability of the formation factor in each sample. While no formal uncertainty analyses were performed for the electrical conductivity methods, the estimated experimental errors are approximately 30% and are far less in magnitude than the differences between maximum and minimum estimated formation factors.

Each sample tested displayed some degree of spatial variability in the formation factors derived from adjacent sections of core; the degree of variability is generally greater though for the breccias that are characterized by obvious heterogeneities than for the more homogeneous breccia and basalt samples. To illustrate this result, two of the more extreme sample results are shown in

Figure 4.4, along with photographs and CT scans. The CT scans illustrate relative densities of the material. As an example, in the Core 7 breccia sample (Figures 4.4a, 4.4b, 4.4c), the high and low formation factors are likely related to the relative proportions of high and low density material in the specific sample section. In contrast, the Core 19 sample appears, in the CT scans, to be comprised of clasts with relatively similar densities, and there is correspondingly less variability in the adjacent measured formation factors (Figures 4.4d, 4.4e, 4.4f).

As can be seen in Figure 4.3, when multiple samples from the same lithologic layer were tested, there were often significant differences between the formation factors for that layer. For example, the Core 8 #1 and #3 samples displayed an average formation factor that was greater than that of the Core 8 #2 and #4 samples by a factor of approximately 1.6. Similarly, the Core 24 #1 sample had a formation factor that was a factor of 1.6 greater than that of the Core 24 #2 sample. These results indicated that there are potentially significant effects of spatial heterogeneities within lithologic layers.

Comparison of the results shown in Table 4.3 and Figure 4.3 illustrate that there are significant effects of spatial heterogeneities with regards to various lithologic layers as well. As noted previously, the various lithologic layers present at the Cannikin test shot location display formation factors that vary by more than one order of magnitude, while the maximum and minimum formation factors found in all of the Amchitka Island samples tested in this study vary by more than two orders of magnitude (on the order of  $10^{-4}$  for the andesite and  $10^{-2}$  for the more porous of the breccia samples).

#### 4.5.3 *Pore network connectivity*

A comparison of the average and the asymptotic values of the formation factors derived by electrical conductivity testing for each sample, as summarized in Table 4.3, indicates that for nearly all of the samples, except for the Core 4 and Core 19 samples, the two values are approximately equal. This observation is in agreement with the results of Löfgren and Neretnieks (2006) for granites. If the pore networks that are connected over distances of 1 cm were not connected over longer distances, than one would anticipate that the average formation factor should be greater than the asymptotic formation factor. This does occur in the Core 4 sample, most likely due to the presence of an observed unconnected fracture.

The Core 19 through-diffusion test results indicated a lower effective porosity for the 0.5 cm thick sample than the measured bulk porosity and a lower formation factor than that measured by electrical methods on a 33 cm sample. As discussed in Benning and Barnes (2008), a lower effective porosity could be caused in part by an unconnected pore network since the through-diffusion sample was only approximately 0.5 cm thick. However, as noted in Section 4.5.1, anion exclusion may also have contributed to this effect (Schön, 1996; Van Loon, *et al.*, 2003; Appelo and Wersin, 2007) as well as the conductivity of the rock material. While basalts and andesites are reported to have similar electrical properties, clay minerals are known to be relatively more conducting (Schön, 1996). Since all of the breccias contain some proportion of clay minerals, some overestimation of the formation factor by electrical methods is likely caused by this influence.

In contrast, the results of the Core 24 through-diffusion experiment did not indicate a substantially lower effective porosity than the bulk measured porosity, which, as discussed and shown in Benning and Barnes (2008), is likely partially caused by the influence of preferential pathways around the edges of clasts. Some of these preferential pathways in a 0.8 cm sample may not be connected over the 5.6 cm sample tested in the modified through-diffusion experiment, and hence the formation factor for the thicker sample is a factor of 0.7 less than the formation factor for the thinner sample. In addition, the good agreement between the formation factors derived by tracer-based methods and that derived by electrical methods could possibly indicate that anion exclusion effects were negligible in this more porous sample, as compared to the Core 19 sample.

#### 4.5.4 Formation factor/porosity relationships

Common practice is to derive an empirical relationship between the formation factor and the porosity of a porous medium, based on Archie's Law (Parkhomenko, 1967; Keller and Ibrahim, 1982). Reimus, *et al.* (2007) determined an empirical relationship for the formation factor that is dependent on not only the porosity, but the permeability as well. The authors, however, noted that their empirically-derived relationship was developed specifically for saturated volcanic rocks from the Nevada Test Site and would not necessarily be the same for other types of rocks. The relationship between the logarithms of the average formation factors derived by the electrical conductivity methods and the porosities is illustrated in Figure 4.5. Because of potential differences between the values derived using different methods, the formation factors derived by



tracer-based diffusion methods and the values for the andesite and Core 87 breccia samples are not included in the determination of the equation for the linear trend indicated in Figure 4.5. The derived equation from this study is:

$$\log(F_f) = 6.9422\phi - 3.442 \quad (4.4)$$

For comparison, the relationship derived by Reimus, *et al.*, (2007) is also illustrated in Figure 4.5. While the empirical relationships illustrated in Figure 4.5 are obviously not identical, it is not unlikely that they may fall within confidence intervals, which were not specified in either study. An important factor to consider is that breccias commonly contain clay minerals, and as noted by Keller and Ibrahim (1982), the conducting properties of clay minerals may result in difficulties in the application of Archie's Law.

Reimus, *et al.* (2007) also derive an equation to estimate the formation factor from the porosity and permeability ( $K_i$ ) data. The equation is given as:

$$\log F_f = (1.42 \pm 1.60) + (1.91 \pm 1.29)\phi + (0.19 \pm 0.089)(\log K_i) \quad (4.5)$$

In these studies, the permeability was measured on only two samples, one derived from Core 19 and one from Core 24. The permeabilities, measured in a fixed-wall type rock permeameter under a simulated overburden pressure of  $1.38 \times 10^4$  kPa (2000 psi), were  $2.17 \times 10^{-14}$  m<sup>2</sup> and  $3.30 \times 10^{-13}$  m<sup>2</sup> for Core 19 and Core 24, respectively. The estimated logarithm of the formation factors from Equation (4.5) for these two cores are compared to the experimentally determined values from both electrical methods and through-diffusion methods in Table 4.4. In all cases, the experimentally determined values are lower than the estimates provided by Equation (4.5). One possible factor causing some of the discrepancy between these values may have been that the permeabilities in these studies were measured under pressure, while it does not appear that the permeability measurements used to derive Equation (4.5) were conducted under pressures (Reimus, *et al.*, 2007), though there was only a 3-4% difference between porosities measured under the same simulated pressure and those measured under atmospheric pressure.

If the data illustrated in Figure 4.4 is expressed in the manner of Archie's Law, the relationship becomes:

$$F_f = 1.20\phi^{3.05} \quad (4.6)$$

In comparison, the exponent in Equation (4.6), which is referred to as the Archie's exponent  $m$ , is considerably higher than the values for  $m$  in published literature for various rock types (Parkhomenko, 1967). Wong, *et al* (1984) have shown that  $m$  is related to the "skewness of the pore-size distribution of the rock." This result would indicate that there is a widely varying distribution of pore sizes in the extrusive volcanic rocks from Amchitka Island, which is not unexpected considering the demonstrated heterogeneities, in particular, of the breccias.

#### 4.5.5 Probability distribution functions of the formation factor

In stochastic models of groundwater flow and contaminant transport, knowledge of the forms of the probability distributions for various parameters is essential. According to Equation (4.2), the matrix diffusion should theoretically have the same form of the probability distribution function (PDF) as the formation factor and should depend on the combined effects of the porosity and the pore structure properties, tortuosity and constrictivity. In an analysis of concrete structures for nuclear containment, Snyder (2003) indicates that the expected distribution of the formation factor for concrete is unknown, though it is likely either normal or lognormal. Towle (1962) notes that the distributions of the pore sizes of rocks are unknown, but that they should be "strongly tied" to the particle size distribution. Lin, Pirie, and Trimmer (1986) found that pores are "usually anisotropic, unevenly distributed and strongly heterogeneous with the formation, and have a skewed logarithmic size distribution;"

The results of each set of adjacent, 1-cm section formation factors derived from electrical conductivity testing, as presented in Figure 4.4 (summary data found in Table 4.3), were statistically tested using either the Shapiro-Wilks W Test when there were less than 50 data points or the D'Agostino K-squared Test when there were greater than 50 data points (Gilbert, 1987) to ascertain the distribution (normal or lognormal) of the formation factor for each core sample. Additionally, when multiple core samples were tested (as with Core 7, Core 8, and Core 24), the combined data sets for each core were analyzed. The distribution of the logarithm (base 10) of the entire data set for all of the samples and layers, as presented in the histogram in Figure 4.6, was also analyzed. The results of the statistical analyses of the PDF's are summarized in Table 4.5.

The results summarized in Table 4.5 indicate that for each core sample, as well as for the combined data sets of different samples from the same core, the PDF's are all normal either at the  $\alpha=0.05$  or the  $\alpha=0.02$  significance level, except for the Core 4 sample. The Core 4 sample PDF, in contrast, fits a lognormal distribution; this result can be explained by the presence of a visible unweathered fracture in the axial direction in the sample. Others have established that the porosity of unconsolidated porous materials follows a normal distribution while the permeability follows a lognormal distribution (Freeze, 1975), and so for the rocks with a distribution of the formation factor that fits the normal distribution, it is likely that the distribution of the porosity plays a dominant role in the formation factor distribution, at least at the scale of these measurements. In contrast, in samples with relatively large-scale heterogeneities, such as the fracture in the Core 4 sample, the distribution may become lognormal as a result of the tendency for extreme values in the resulting data sets.

When all of the geologic layers are considered together, as in Figure 4.6, because of the order of magnitude differences between the formation factors to the depth of the Cannikin test shot, the distribution of the subsurface as a whole in the Cannikin test shot vicinity can be described by a lognormal distribution. This result is in concurrence with the high  $m$ -factor in Archie's Law, which, as noted in Section 4.5.4, indicates a high-skewness in the formation factor data for the site. Some caution is noted however, because though the entire set statistically can be described by a lognormal distribution at the  $\alpha=0.02$  significance level, the lognormal distribution hypothesis is rejected at the  $\alpha=0.05$  significance level, indicating that the D'Agostino test statistic is borderline. This may be attributed to the sparseness of data with values around those of the Core 24 values.

#### 4.5.6 *Diffusion in the Amchitka Island subsurface*

The results presented in the preceding are expected to enhance the understanding of the fate and transport of radionuclides at Amchitka Island, Alaska. Regarding the effects of scale on diffusion, as presented in Section 4.5.1, it does not appear that scale effects are a significant concern for estimating diffusivities at the island, at least at the scale of the laboratory measurement, up to 42 cm in length. While there are some effects of scale, these are mostly limited to diffusion lengths of approximately 6 cm. Overall, at the scale of the laboratory measurements, the pore networks for the basalts and breccias studied appear to be well-connected, in agreement with the results for the granites studied by Löfgren and Neretnieks

(2006). There should, however, be some caution in studying samples that are too small such that pores become connected that would not be connected at larger scales and such that the influence of induced microcracks is too large, as was noted by Reimus, *et al.* (2007). This effect was observed in these investigations in the through-diffusion experiments, though other than the potential effect on the measured porosity in the Core 19 sample, the impacts are generally small in comparison to the heterogeneities observed between geologic layers. In comparison of the results of these investigations to those of previous investigations into diffusion at Amchitka Island, however, the impact of using too small a sample are more pronounced.

The results of these investigations reveal, for the samples investigated, formation factors ranging from  $1.3 \times 10^{-4}$  to  $5.4 \times 10^{-2}$  for the island and from  $7.4 \times 10^{-4}$  to  $3.3 \times 10^{-2}$  for the Cannikin test shot location. For the basalts, the estimated formation factors are between  $1.5 \times 10^{-3}$  and  $2.3 \times 10^{-3}$ , which is much lower than the range estimated for basalts in Brown's (2000) study of  $3.6 \times 10^{-2}$  and  $4.2 \times 10^{-1}$ . These investigations indicate a much wider range of formation factors for the breccias at the island of between  $7.4 \times 10^{-4}$  to  $5.4 \times 10^{-2}$ , as compared to the range for breccias given by Brown of  $1.6 \times 10^{-2}$  to  $7.5 \times 10^{-2}$  (though it is noted that in Brown's investigations fewer breccia samples were analyzed). In comparing these results, some consideration should be given to the sample sizes used in Brown's study, which were much smaller than those used in these investigations. Therefore, it is likely that the use of small samples could allow pores to become connected that would otherwise not be connected in larger samples, significantly contributing to the overestimation of the formation factors for both the basalts and breccias in Brown's study.

The results shown in Figure 4.7 illustrate the porosity and formation factor profile with depth at the Cannikin test shot location, to the approximate depth of the Cannikin detonation. The profile suggests a strongly layered subsurface with regards to the variability in both the formation factor, as discussed in the preceding, and the bulk porosity, which ranges from 11.5% to 27.1%. In a previous groundwater model for the island, Wheatcraft (1995) recommended that that model could be improved by the consideration of a layered geologic system. Later groundwater models by Hassan and Chapman (2006) and Wagner (2007) applied the effective porosity profile from magnetotelluric (MT) data illustrated in Figure 4.8. The bulk porosity data appears to closely match the Archie's  $m=2$  line for the MT profile; though because of the scale of measurements in the MT profile, the profile is smoothed as compared to the laboratory porosity measurements. Overall, the bulk porosities tend to be higher than those used in the groundwater models (Wagner,

2007); however, the estimate of the effective porosity derived from the Core 19 through-diffusion experiment is less than the  $m=1.5$  value that was applied in the groundwater model at that location.

Wagner (2007) considered the influence of an andesite sill layer in the groundwater model for the Long Shot (LS) test site. This sill is characterized by an extensive fracture network that yields a high hydraulic conductivity for the layer. When the influence of this sill was considered, the estimated groundwater travel time (no diffusion or sorption was considered) to the ocean floor from the test cavity was reduced from an estimated 1400 - 4700 years to an estimated 400 - 1400 years, indicating the importance at that site of a layered approach to modeling. While LS-vicinity cores were not available for these investigations, the estimated matrix porosity and matrix formation factor for an andesite core sample derived from the Milrow vicinity are very low, at 9% and  $1.3 \times 10^{-4}$ , respectively, for the site. This suggests that there is a low potential for diffusion and subsequent retardation of radionuclides in that layer, and the radionuclide transport rates would not be significantly lowered from the groundwater transport rates.

#### 4.6 CONCLUSIONS

The investigations indicate that there is some effect of scale on measured intrinsic diffusion coefficients and formation factors, but these effects are generally small in comparison to variability between lithologic layers. These effects are also generally limited to approximately 6 cm for most samples and are well-correlated with observed heterogeneous features. Similar to the results of Löfgren and Neretnieks (2006) for granites, the pore structures of the breccias and basalts present in the subsurface at Amchitka Island appear to be well-connected at the scale of laboratory measurements (up to 42 cm in length). For most of the samples investigated, the average formation factor for adjacent 1-cm sections of rock is approximately equal to the asymptotic value of the formation factor for increasing sample lengths, thereby implying that an adequate estimate for even the most heterogeneous of the breccia samples can be obtained either by conducting tests on multiple small samples or by conducting tests on longer samples, which allows for flexibility in experimental design. An important conclusion resulting from this study is that there is a potential for the estimated formation factor to be misrepresented by an order of magnitude if multiple samples are not tested.

For individual geologic layers, the investigations indicate that the probability distribution function of the formation factor is normal, except when the sample is influenced by features with different properties than the surrounding matrix properties (e.g., an unconnected and unweathered fracture). However, the probability distribution function for the formation factor throughout the depth of the Cannikin vicinity subsurface shows a lognormal distribution, due to the order of magnitude differences between lithologic layers. The large skewness of the distribution is corroborated by the high  $m$ -factor in Archie's Law for the relationship between the porosity and formation factor for the Amchitka Island samples. An understanding of the probability distribution function is essential to stochastic modeling efforts.

The intrinsic diffusion coefficients and formation factors derived in these studies are much lower than those derived in previous, more limited diffusion studies for Amchitka Island. The formation factor and porosity profiles for the Cannikin test site show a strongly layered subsurface with a large spatial variability found in both parameters. The results of these investigations are anticipated to reduce some of the uncertainties associated with the radionuclide transport modeling at the island.

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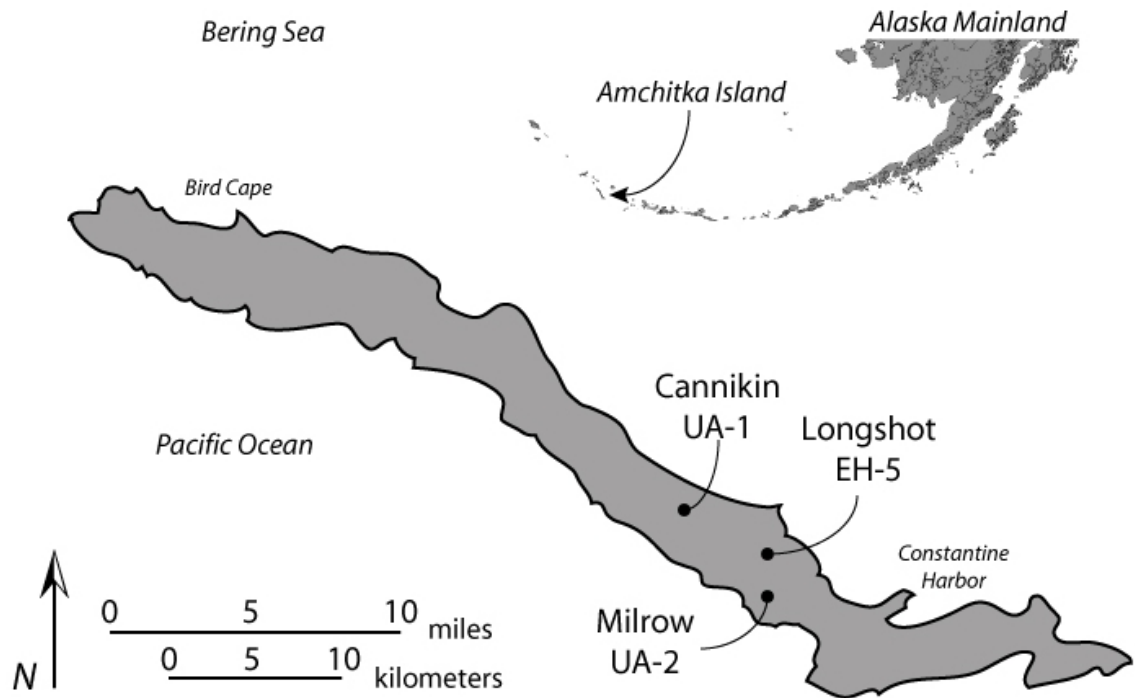
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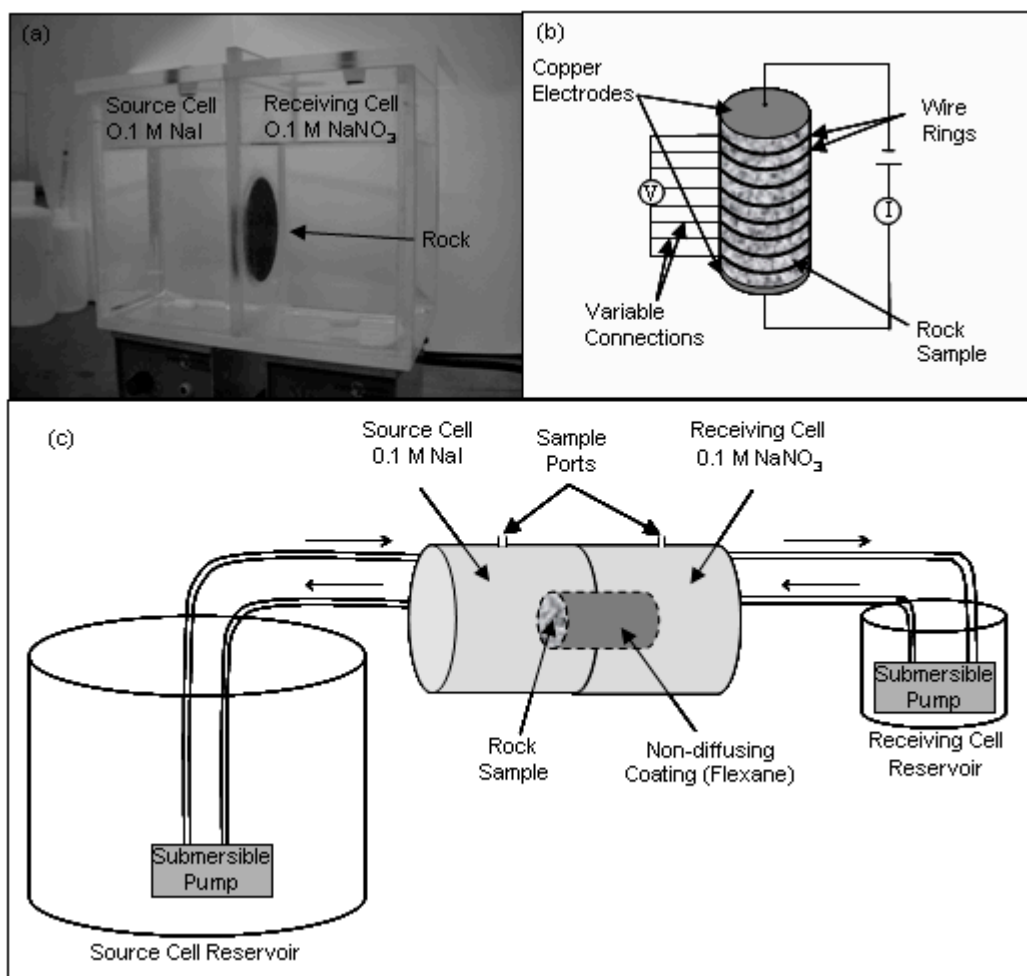
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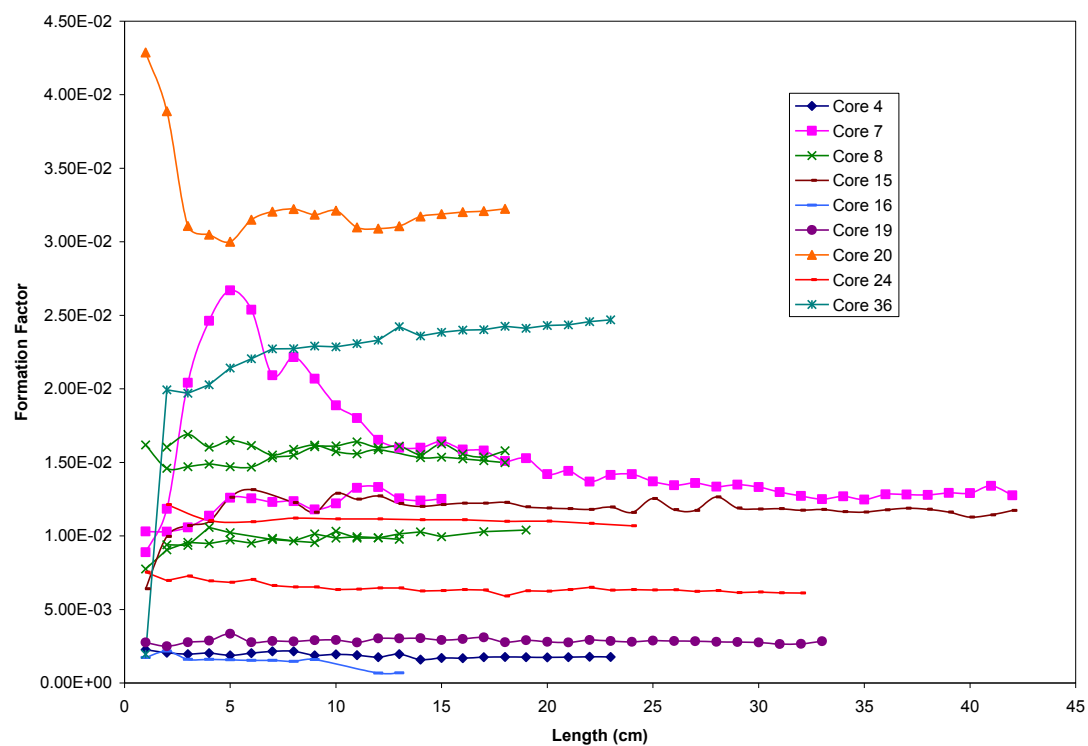
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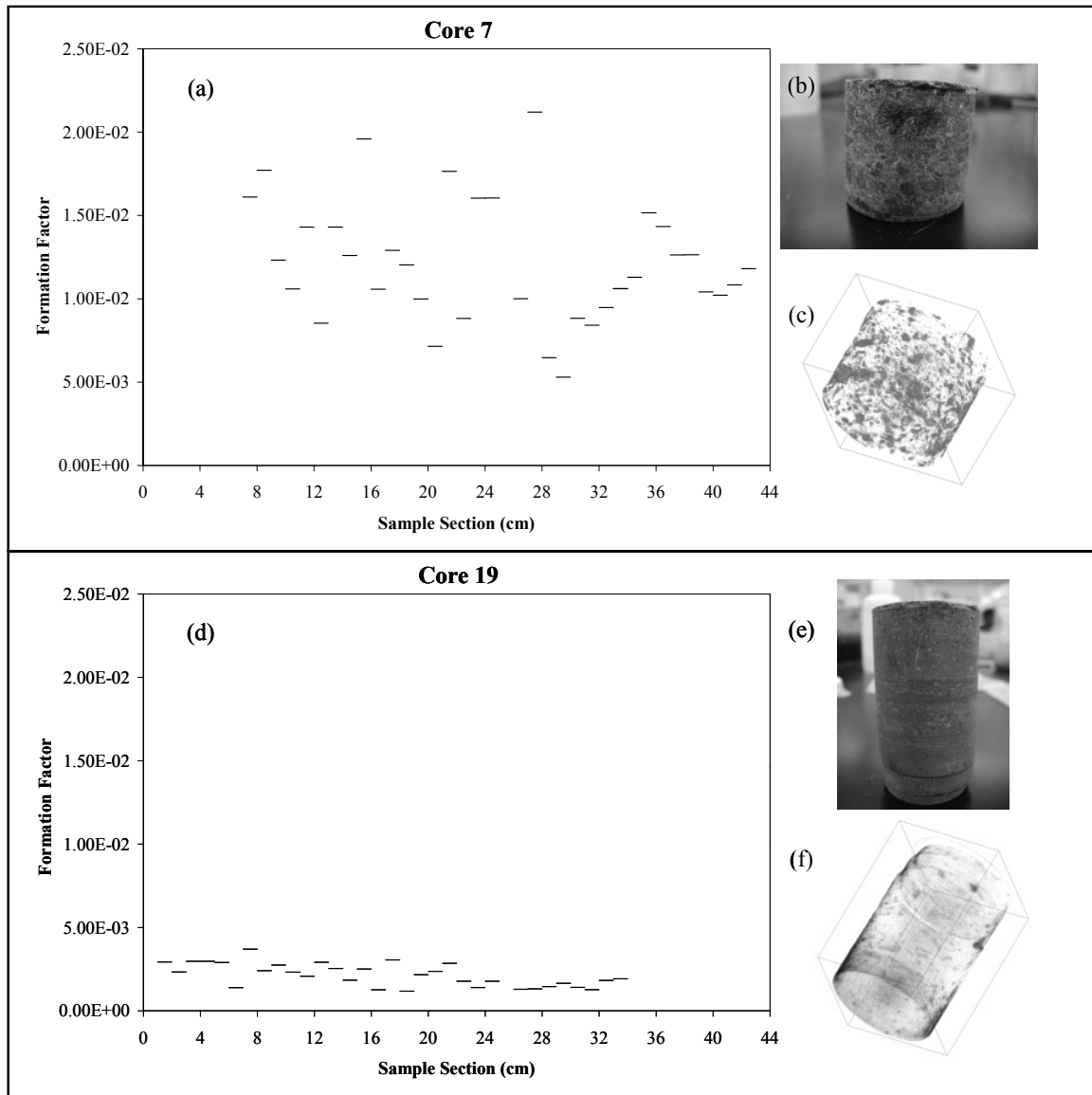
**Figure 4.1** Map of Amchitka Island, Alaska showing the location of the three underground nuclear tests: Long Shot, Milrow and Cannikin.



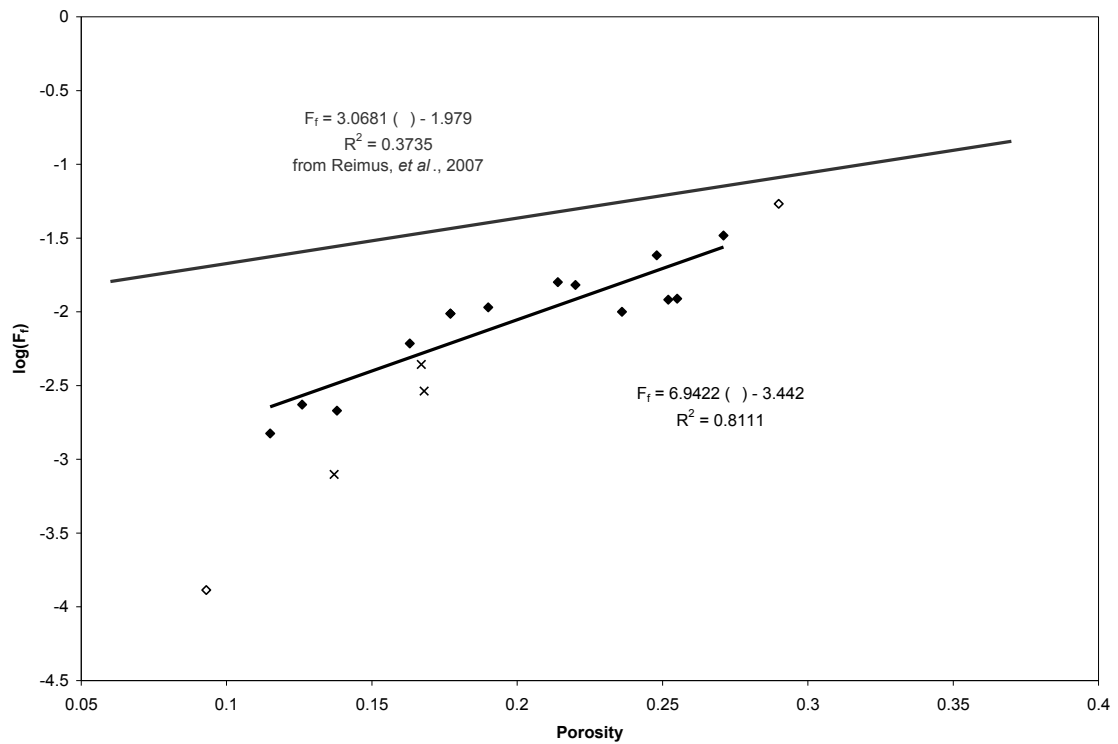
**Figure 4.2** Illustrations of experimental apparatus for: (a) through-diffusion (b) electrical conductivity (c) modified through-diffusion.



**Figure 4.3** The influence of sample length on the formation factor measured by electrical conductivity testing.

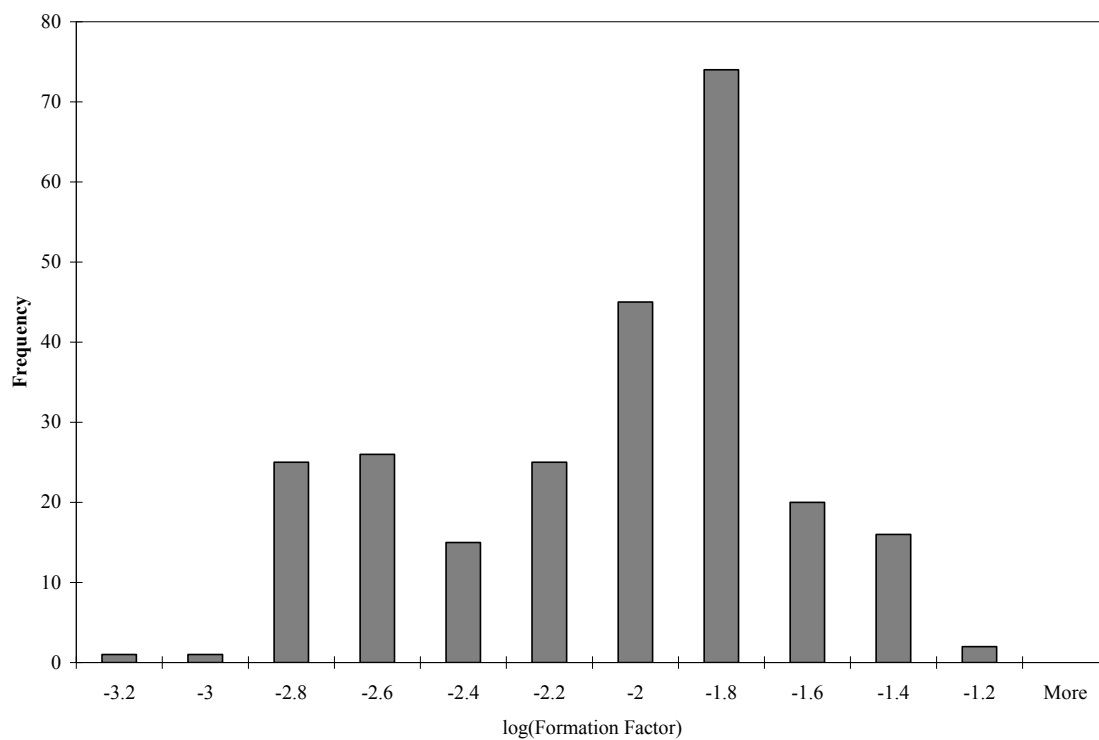


**Figure 4.4 Spatial variability of the measured formation factor across 1-cm thick adjacent sample sections for (a) Core 7 and (d) Core 19. Photographs of adjacent 51-mm diameter core samples for (b) Core 7 and (e) Core 19. 3-D view of samples produced by X-ray CT imaging, with dark colors represent high densities, 51 mm diameter samples of (c) Core 7 and (f) Core 19.**



**Figure 4.5 Formation factor as a function of porosity. The diamonds denote formation factors measured by electrical conductivity and are included in the regression analysis, the open circles represent formation factors measured by electrical conductivity in the preliminary investigations, and the x's represent formation factors measured by tracer-based methods.**





**Figure 4.6 . Histogram of the logarithm (base 10) of the formation factors measured in this study on all core samples at adjacent 1-cm sample sections using electrical methods.**

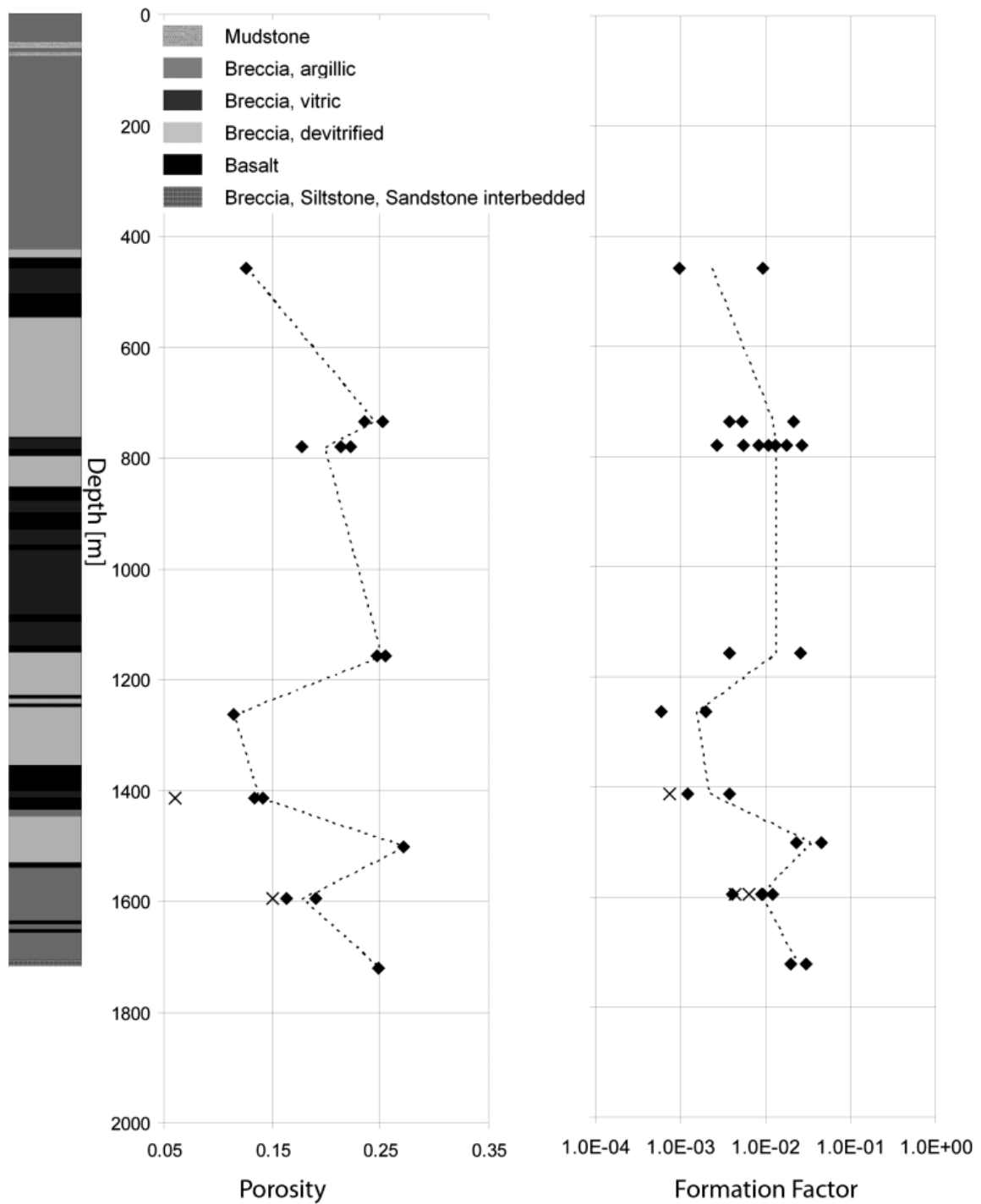
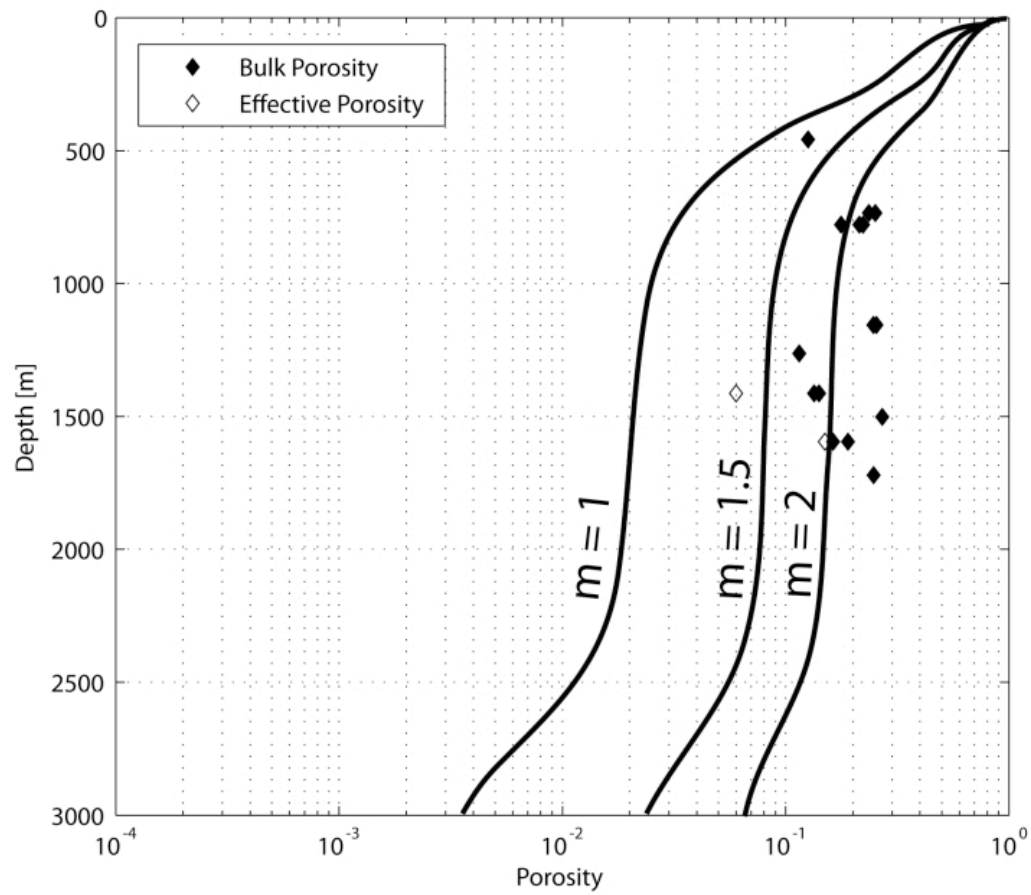


Figure 4.7 The variation of the measured porosities and formation factors with depth of sample origin, compared to the UAE-1 (Cannikin vicinity) core log, displaying basic categories of rock types encountered. The diamonds represent the porosities and the maximum and minimum formation factors measured by water saturation and electrical methods, respectively. The x's represent the

effective porosities and formation factors measured by tracer methods. The dashed lines connect the average measurements for each core sample.



**Figure 4.8** Comparison of the depth profile of the porosities measured in these studies to the profile of the porosities derived in magnetotellurics studies (from Unsworth, *et al.*, 2007).

**Table 4.1 . Location and lithologic description of core samples from the UAe-1 drill hole analyzed in this study, from Gard, *et al.*, 1969a,b.**

| Core | Depth<br>Below Grade<br>(m) | Lithologic Description  |
|------|-----------------------------|---|
| 4    | 456 – 459                   | Basalt, dark gray, dense, massive. Contains small feldspar and pyroxene phenocrysts. Core shows discontinuous fractures well healed with chalcedony.  |
| 7    | 734 – 737                   | Breccia, greenish-black, dense, devitrified. Matrix contains basalt fragments, a few purple andesite fragments as large as 7.5 cm, a few green chloritized rock fragments, and some pyrite and pyroxene crystals as large as 5 mm. Average fragments size 5 mm.   |
| 8    | 768 – 781                   | Breccia, black, slightly devitrified, very dense and brittle. Devitrified greenish-black matrix contains resinous vitric spherulites and feldspar laths. Black vesicular glass fragments average 2.5 cm and contain radially fibrous zeolites in vesicles. Core contains one rectangular fragment of fine-grained light-gray diorite. |
| 15   | 1155 – 1158                 | Breccia, black, devitrified. Fragments devitrified, average size 5 mm. One large (20 inch) basalt fragment in core is medium-gray, very fine grained. Basalt has vesicles filled with zeolites and displays chilled margin.   |
| 16   | 1228 – 1236                 | Basalt, aphanitic to fine-grained, porphyritic with phenocrysts of pyroxene (augite). Felted groundmass of plagioclase and glass.   |
| 19   | 1412 – 1414                 | Breccia, greenish-black, very dense, brittle, altered. Matrix contains small (<12 mm) aphanitic basalt fragments. Zeolites and chalcedony distributed throughout; some pyroxene crystals in matrix.   |
| 20   | 1501 – 1503                 | Breccia, greenish-gray, soft, devitrified, argillized. Zeolites and chalcedony throughout. Fragments are argillized glass and basalt. Pyroxene crystals in matrix.  |
| 24   | 1593 – 1596                 | Breccia, mottled pale-green and very light gray, propylitized. Lithic fragments range in size from 1 mm to 1 cm and are subrounded to rounded, predominantly basalt. Fine-grained clayey matrix, constitutes about 10 percent of rock and contains rare pyroxene crystals.  |
| 36   | 1710 – 1730                 | Interbedded sandstone and fine-grained breccia. Composed of volcanic rock fragments, minute augite grains, and opaque minerals. Whole rock is propylitized.   |

**Table 4.2 Comparison of formation factors and porosities derived from different sample lengths and different methods for two breccia samples.**

| Sample  | Length<br>(cm) | Porosity<br>(%) | Method            | Formation Factor  | Method                     |
|---------|----------------|-----------------|-------------------|---|----------------------------|
| Core 19 | 0.5            | 13.7            | Water Balance     | $7.4 \times 10^{-4}$  | Through-Diffusion          |
|         |                | 6.0             | Through-Diffusion |   |                            |
|         | 6.4            | 13.8            | Water Balance     | --  | Modified Through-Diffusion |
|         | 33             | 13.4            | Water Balance     | $1.2 \times 10^{-3} - 3.7 \times 10^{-3}$<br>$2.8 \times 10^{-3}$ (average) | Electrical Conductivity    |
| Core 24 | 0.8            | 16.8            | Water Balance     | $6.4 \times 10^{-3}$  | Through-Diffusion          |
|         |                | 15.0            | Through-Diffusion |   |                            |
|         | 5.6            | 16.7            | Water Balance     | $4.4 \times 10^{-3}$  | Modified Through-Diffusion |
|         | 28             | 19.0            | Water Balance     | $9.2 \times 10^{-3} - 1.2 \times 10^{-2}$<br>$1.1 \times 10^{-2}$ (average) | Electrical Conductivity    |
|         | 33             | 16.3            | Water Balance     | $4.1 \times 10^{-3} - 8.9 \times 10^{-3}$<br>$6.1 \times 10^{-3}$ (average) | Electrical Conductivity    |

**Table 4.3 The maximum, minimum, and average formation factors derived from electrical conductivity testing on adjacent axial sections of core samples (with the factor as the ratio of the maximum to minimum formation factor); the asymptotic values of the formation factor, defined here by variations of less than +/- 10%, and the lengths required to achieve the asymptotic value.**

| Sample                   | Length<br>(cm) | Porosity | Formation Factor x 10 <sup>2</sup> |         |                     |         |            | Length to<br>Asymptote<br>(cm) |
|--------------------------|----------------|----------|------------------------------------|---------|---------------------|---------|------------|--------------------------------|
|                          |                |          | Minimum                            | Maximum | Factor<br>(max/min) | Average | Asymptotic |                                |
| UAe-2<br>Andesite        | 2              | 0.093    | --                                 | --      | --                  | 0.013   | --         | --                             |
| Core 16<br>Basalt        | 13             | 0.115    | 0.058                              | 0.20    | 3.5                 | 0.15    | 0.16       | 3                              |
| Core 4<br>Basalt         | 23             | 0.126    | 0.096                              | 0.91    | 9.4                 | 0.23    | 0.17       | 15                             |
| Core 19<br>Breccia       | 33             | 0.138    | 0.12                               | 0.37    | 3.1                 | 0.21    | 0.28       | 6                              |
| Core 24 (2)<br>Breccia   | 32             | 0.163    | 0.41                               | 0.89    | 2.2                 | 0.61    | 0.63       | 7                              |
| Core 24 (1)<br>Breccia * | 24             | 0.190    | 0.92                               | 1.2     | 1.3                 | 1.0     | 1.1        | 4                              |
| Core 8 (4)<br>Breccia    | 18             | 0.177    | 0.27                               | 1.8     | 6.6                 | 0.97    | 0.95       | 6                              |
| Core 8 (2)<br>Breccia    | 13             | 0.177    | 0.82                               | 1.3     | 1.6                 | 0.97    | 0.95       | 2                              |
| Core 8 (3)<br>Breccia    | 18             | 0.214    | 1.1                                | 2.7     | 2.5                 | 1.6     | 1.6        | 2                              |
| Core 8 (1)<br>Breccia    | 18             | 0.222    | 0.55                               | 2.7     | 4.9                 | 1.5     | 1.6        | 1                              |
| Core 7 (2)<br>Breccia    | 15             | 0.236    | 0.37                               | 2.1     | 5.7                 | 1.0     | 1.3        | 5                              |
| Core 7 (1)<br>Breccia    | 42             | 0.252    | 0.53                               | 2.1     | 4.0                 | 1.2     | 1.3        | 20                             |
| Core 36<br>Breccia       | 23             | 0.248    | 2.0                                | 3.0     | 1.5                 | 2.4     | 2.4        | 6                              |
| Core 15<br>Breccia       | 42             | 0.255    | 0.38                               | 2.6     | 6.7                 | 1.3     | 1.2        | 4                              |
| Core 20<br>Breccia       | 18             | 0.271    | 2.3                                | 4.6     | 2.0                 | 3.3     | 3.2        | 3                              |
| UA-1, C87<br>Breccia     | 4              | 0.29     | --                                 | --      | --                  | 5.4     | --         | --                             |

\* A 2-cm spacing was used for the Core 24 (1) sample.

**Table 4.4 The value of  $\log(F_f)$  derived from Equation (4.5) and measured porosities and permeabilities (Reimus, *et al.*, 2007) compared to experimentally determined values derived from both electrical and tracer-based methods.**

| Method                             | $\log(F_f)$      |                  |
|------------------------------------|------------------|------------------|
|                                    | Core 19          | Core 24          |
| Equation (5)                       | $-1.03 \pm 0.49$ | $0.60 \pm 0.75$  |
| Electrical Conductivity Experiment | -2.7             | $-2.1 \pm 0.1$   |
| Through-Diffusion Experiment       | -3.1             | $-2.45 \pm 0.05$ |

**Table 4.5 Summary of statistical tests to describe PDF of the formation factor from the data for each sample.**

| Sample             | Number of Data Points, n | PDF at $\forall=0.05$ | PDF at $\forall=0.02$ | Mean    | Standard Deviation |
|--------------------|--------------------------|-----------------------|-----------------------|---------|--------------------|
| Core 4 Basalt      | 23                       | not lognormal         | lognormal             | -6.23 * | 0.56**             |
| Core 7 #1 Breccia  | 36                       | normal                | normal                | 1.21E-2 | 0.37E-2            |
| Core 7 #2 Breccia  | 15                       | normal                | normal                | 1.16E-2 | 0.38E-2            |
| Core 8 #1 Breccia  | 17                       | normal                | normal                | 1.49E-2 | 0.50E-2            |
| Core 8 #2 Breccia  | 13                       | normal                | normal                | 9.70E-3 | 1.5E-3             |
| Core 8 #3 Breccia  | 16                       | normal                | normal                | 1.59E-2 | 0.38E-2            |
| Core 8 #4 Breccia  | 15                       | normal                | normal                | 9.72E-3 | 3.8E-3             |
| Core 15 Breccia    | 39                       | normal                | normal                | 1.27E-2 | 0.48E-2            |
| Core 16 Basalt     | 12                       | normal                | normal                | 1.46E-3 | 0.36E-3            |
| Core 19 Breccia    | 33                       | normal                | normal                | 2.14E-3 | 0.68E-3            |
| Core 20 Breccia    | 18                       | normal                | normal                | 3.28E-2 | 0.56E-2            |
| Core 24 #1 Breccia | 12                       | normal                | normal                | 1.07E-2 | 0.08E-2            |
| Core 24 #2 Breccia | 32                       | normal                | normal                | 6.10E-3 | 1.1E-3             |
| Core 36 Breccia    | 22                       | normal                | normal                | 2.42E-2 | 0.29E-2            |
| Core 7 all         | 51                       | normal                | normal                | 1.20E-2 | 0.37E-2            |
| Core 8 all         | 61                       | normal                | normal                | 1.28E-2 | 0.47E-2            |
| Core 24 all        | 44                       | normal                | normal                | 7.36E-3 | 2.3E-3             |
| All Data           | 303                      | not lognormal         | lognormal             | -4.82 * | 0.94 **            |

\* The mean is given as the mean of  $\ln(F_f)$  to characterize the lognormal distribution.

\*\* The standard deviation is given as the standard deviation of  $\ln(F_f)$  to characterize the lognormal distribution.



## **5 AMCHITKA ISLAND, ALASKA: MOVING TOWARDS LONG TERM STEWARDSHIP**

### **Abstract**

Amchitka Island, Alaska, is a historical underground nuclear test site. Three underground tests were conducted there by the United States Atomic Energy Commission, now US Department of Energy (USDOE), between 1965 and 1971. These were Long Shot, an 80 kiloton detonation; Milrow, a 1 megaton detonation; and Cannikin, a 5 megaton detonation. Subsequent to these tests, several scientific assessments have been conducted regarding the impacts of the tests on the terrestrial and marine environments surrounding the island. However, many citizens and groups still voice concerns over the potential for detrimental effects on human and ecological health. In its responsibility for the long term protection of human and ecological health consequent to its nuclear programme, USDOE has recently prepared a plan for the long term surveillance and monitoring of the site. The purpose of this paper is to summarise the history of the island, specifically with regards to its use as a nuclear test site, to summarise the results of investigative activities following testing, to summarise USDOE's plan for surveillance and monitoring, and to offer the authors' viewpoints on the long term stewardship of the island. The authors deemed the stewardship plan to be essentially protective of human and ecological health; however, they recommend a stronger commitment to site oversight and review, as well as to future research, for addressing uncertainties remaining at the island.

Benning, J.L., D.L. Barnes, J. Burger, J.J. Kelley. 2008. Amchitka Island, Alaska: moving towards long term stewardship, *Polar Record*, in press.

## 5.1 INTRODUCTION

Amchitka Island is located in the centre of the Aleutian Island chain of Alaska, which divides the Bering Sea to the north from the Pacific Ocean to the south. The area is known for its harsh climate, characterised by frequent rain and high winds, as well as its prolific fishing grounds. In the span of human history, the island has moved from semi-permanent native settlements, through Russian occupation, wildlife refuge, military occupation, to a nuclear and subsequently, post-nuclear test site. Now, in the post-nuclear test era, Amchitka Island remains an environmental concern to many interested parties, including subsistence communities in the vicinity of the island, commercial fishing industries, the State of Alaska, and the United States Fish and Wildlife Service, due to radionuclides released in the subsurface with the underground blasts. In order to address these concerns, the US Department of Energy (USDOE) has recently developed a plan for the long term stewardship of the island. The purpose of this paper is to summarise the history of the island, specifically with regards to its use as a nuclear test site, to summarise the results of investigative activities following testing, to summarise USDOE's plan for surveillance and monitoring, and to offer the authors' viewpoints on the long term stewardship of the island. Due to the environmental and health concerns regarding the potential impacts of the nuclear detonations, there is a need to provide a record of the activities, the results of assessments, information on the long term management plan, and a review of the remaining uncertainties for the Polar and sub-Polar communities.

## 5.2 SITE DESCRIPTION

Amchitka Island, Alaska, is located at lat. 51.5°N and long. 179°E, and lies in the Aleutian Island chain, almost equidistant from the Alaskan and Russian mainlands (see Figure 5.1). The long, narrow island is situated along a northwest-southeast plane. It is approximately 65 km (40 miles) long and 2 to 7 km (1–4 miles) wide (Merritt 1977a). It is part of the Rat Islands group of the Aleutians, which also includes the islands of Kiska, Segula, Rat, Khvostof, Davidof, Little Sitkin, and Semisopochnoi.

The Aleutian Island chain was formed by the volcanic action of the Aleutian volcanic arc, where the islands exist as the peaks of a submerged mountain range lying parallel to a submarine trench, reaching a depth of up to 7600m. Amchitka, like most of the islands, is composed entirely of volcanic rocks, encompassing andesitic to latitic breccias, glassy breccias and basaltic pillow

lavas (Carr and others 1971; Merritt and Fuller 1977; Eichelberger and others 2002). The island is 'part of a small crustal block being torn apart by oblique subduction - and therefore one of the least stable tectonic environments in the United States' (Eichelberger and others 2002). Earthquakes are common in this region, and earthquakes over magnitude 8 have been reported with relative frequency (Eichelberger and others 2002). In 2003, there were two earthquakes over magnitude 7 centred in the Rat Islands; a 7.1 magnitude on 17 March and a 7.8 magnitude on 17 November (USGS 2003a, 2003b). In 2007, a magnitude 7.2 earthquake centred in the Andreanof Islands, 116 km from Amchitka Island, occurred on 19 December (USGS 2008).

The marine environment surrounding Amchitka is rich in nutrients as a result of cold ocean upwellings and hosts a rich and diverse ocean life. The region is important for subsistence and commercial catches, walleye pollock *Theragra chalcogramma*, pacific cod *Gadus macrocephalus*, halibut *Hippoglossus stenolepis*, rock sole *Hippoglossus stenolepis*, rockfishes *Sebastes spp.*, salmon *Oncorhynchus*, and king crab *Paralithodes camtschaticus*. Many marine mammals, such as whales, seals, sea otters, and sea lions are prolific (Polar Research Board 1996). The island itself is host to 131 species of birds, some resident and some migratory, including species such as the Lapland larkspur, *Calearius lapponicus*, bald eagle *Haliaeetus laucocephalus*, peregrine falcon *Falco peregrinus*, and cormorants *Phalacrocorax*. The only terrestrial mammals historically present on the island are introduced species, the blue fox *Alopex lagopus*, which was introduced for economic endeavours and later eradicated, and the Norway rat *Rattus norvegicus*, which was accidentally introduced during World War II and still persists in great numbers on the island (Breechbill 1977; Merritt 1977b; White and others 1977; Burger and others, 2006a).

The total human population of the Aleutian Islands on 1 July 2007 was 7490 (US Census Bureau 2007). Though historically Amchitka Island has hosted a population, there has not been a non-military continuous occupation of the island since the late 1800's. The nearest current non-military population to Amchitka Island is located on Atka Island, approximately 450km (270 miles) away, with a population of 158 in 2006 (Merritt 1977a; US Census Bureau 2006).

There are currently 51 pending native claims referring to over 100 sites on Amchitka Island, generally related to cemetery and historical sites as provided for by the 1971 Alaska Native Claims Settlement Act (United States, Public Law 1971) and the Alaska National Interest Lands

Conservation Act (United States, Public Law 1980). Due to the island's historical use as a nuclear testing facility, settlements would not be allowed on the island; however, the conveyance of these claims would alter the basis of the island's use and thus, the need for institutional controls on the island (USDOE 2008).

### 5.3 HISTORY

#### 5.3.1 *Pre-nuclear era (until 1965)*

The Aleutian people settled in the Aleutian islands 10,000 years ago (Bernstein and others 1982). On Amchitka Island, archeological sites date back 3600 to 4600 years. Of the Rat Islands, Amchitka Island hosts the largest number of settlement sites, 73 of the total 86 in the island group, and estimates indicate that the island may have been home to more than 1,100 people (McCarthy 1977).

Russian exploration into the Aleutians began in 1743, and the first documented account of Russian landing on Amchitka Island was Vorob'ev's exploration of 1760 to 1763. The pre-contact population of the Aleutians is estimated to have been between 12,000 and 15,000; this was reduced, by exploitation and disease to fewer than 4000 by 1830 (Merritt 1977b). On Amchitka Island, the Russian hunters forced the relocation of the island's inhabitants, and sometime after 1821, 85 Amchitkans were moved to Adak and Atka. Some of the Amchitkans may have been returned sometime after, but records indicate that the last permanent native settlement on Amchitka was abandoned by 1849 (Merritt 1977b; Kohlhoff 2002).

The United States purchased the Alaskan territory from Russia in 1867, by which time, the Aleut population had declined to around 2,000. In 1913, President Taft signed an executive order that created the Aleutian Islands Reservation, whereby the islands were designated 'as a preserve and breeding ground for native birds, for the propagation of reindeer and fur bearing animals, and for the encouragement and development of fisheries.' However, the order also stated that '[t]he establishment of this reservation shall not interfere with the use of the islands for lighthouse, military, or naval purposes....' In 1940, the reserve was renamed the Aleutian Islands National Wildlife Refuge (Merritt 1977b).

In June 1942, World War II came to Alaska when the Japanese bombed military installations in Dutch Harbor and occupied Attu and Kiska Islands. These attacks and invasions by an enemy on

US soil prompted the Aleutian campaign, involving US and Canadian troops, of 1942 and 1943 (Merritt and Fuller 1977; Bernstein and others 1982; Garfield 1995; Kohlhoff 2002). During the Aleutian campaign, the Aleutian population and culture was further eroded and irrevocably damaged by the US government's relocation and internment of Aleuts and Pribilof Islanders from 1942 to 1943; following internment, many villages were never re-established (Bernstein and others 1982).

On 12 January 1943, 2100 American engineers and army troops landed on Amchitka Island following scouting activities in December 1942, which included the bombing of the abandoned village. A landing strip was constructed soon after, marking the beginning of the island's use as a military site. An estimated maximum 15,000 military personnel would eventually be stationed at Amchitka prior to military evacuation in 1950. (Merritt 1977b; Garfield 1995; USDOE 1998).

### 5.3.2 *Nuclear Era*

Amchitka Island was used as an underground test site from 1965 until 1971. The energy released in the three tests conducted there represents roughly 16% of the energy released during the entire US underground nuclear testing programme, and the Cannikin test was the largest ever detonated in the programme (US Congress 1989; Robbins and others, 1991; Norris and Arkin, 1998; USDOE 2006).

In general, when an underground nuclear device is detonated, the billions of atoms contained in the bomb release their energy nearly instantaneously, creating pressures of several billion Pascals and temperatures around 100 million °C. Surrounding rock and metal bomb material are vaporised, and the gas pressures created will begin to form a cavity. Seismic waves similar to those released by an earthquake will propagate outward from the detonation. Within a few seconds after detonation, molten rock surrounding the detonation cools and solidifies in the bottom of the cavity. Eventually, gas pressures decrease in the cavity to a level that will no longer support the overburden. At this point, the overlying rock will break and collapse into the cavity, creating rubble and a chimney, which may or may not reach ground surface. This collapse may take hours to months after detonation. Much of the radioactive material released by the detonation will become trapped in the vitric, or cooled molten, material, however, some will partition between gas, liquid, and solid phases underground. Some radionuclides are highly sorbed onto rubble and other rock material, but some of the more soluble nuclides may infiltrate

into groundwater and be transported (US Congress 1989; IAEA 1998a). This process is illustrated in Figure 5.2.

#### 5.3.2.1 Long Shot

In 1963, the US and Soviet governments signed the Limited Test Ban Treaty, which prohibited above ground and underwater testing of nuclear weapons. However, because at the time, there was no existing technology to detect underground nuclear tests, this treaty did not limit underground testing. The US Department of Defense (DOD) initiated the Vela Uniform Project in an attempt to develop seismic detection technology that would enable the detection of underground detonations. Under this project, several underground tests were performed in the US between 1963 and 1971, most of them at the Nevada Test Site. However, Amchitka Island became the location of one of these tests (Merritt and Fuller, 1977; US Congress 1989; Kohlhoff 2002; USDOE 2006).

On 29 October 1965, the 80 kiloton nuclear bomb known as Long Shot was detonated at a depth of 720 m (2350ft) below ground surface. Long Shot was conducted as a part of the Vela Uniform project, and was conducted shortly after an 8.7 magnitude earthquake in the vicinity. The main impetus for the shot was to determine whether or not the then current monitoring technology could differentiate between natural seismic activity and an underground nuclear explosion. The DOD conducted the Long Shot test and had initially planned to conduct the test in secret; however, due to the statutory responsibility of the Atomic Energy Commission (AEC), the AEC involvement was required and the public was informed prior to the test (Merritt and Fuller 1977; Kohlhoff 2002; USDOE 2006).

#### 5.3.2.2 Milrow

In 1966, the AEC began to search for alternative test sites for high yield weapons, as population and an increasing number of high rise buildings in Las Vegas, Nevada was beginning to cause safety concerns for the use of the nearby Nevada Test Site. Amchitka Island was selected as an alternate test site, and the United States Geological Survey (USGS) began geological investigations that year on behalf of the AEC at six sites on the island (named Sites A, B, C, D, E, and F) (Merritt 1977b; Kohlhoff 2002).

The Milrow test shot was detonated at Site B of Amchitka Island on 2 October 1969 at a depth of 1218m (4000ft) below ground surface. The approximately 1 megaton nuclear device detonated was conducted as a seismic calibration test to determine if Amchitka Island could sustain the detonation of a higher yield Spartan anti-ballistic missile warhead (Fuller and Kirkwood 1977; US Congress 1989).

#### 5.3.2.3 Cannikin

Following the Milrow test shot, the AEC determined that Amchitka Island could sustain the detonation of a higher yield weapon, and planning for the larger test shot, Cannikin, under the Safeguard Ballistic Missile Defense Program ensued. In 1970, the National Environmental Policy Act (NEPA) was passed, and as a result, the Cannikin test required an Environmental Impact Statement (EIS) as part of the planning. There was much political debate and public protest to the test, as described by Kohlhoff (2002), including two law suits and the formation of Greenpeace and their subsequent purchase of a boat and near attempt to witness the detonation. However, despite protests, on 6 November 1971, the Cannikin test detonated an approximately 5 megaton Spartan warhead at a depth of 1790m (5875ft) below ground surface (US AEC, 1972; Claassen, 1978; US Congress, 1989; USDOE, 2006).

Unique to the Cannikin test shot, a re-entry drill hole, UA-1-P1, was advanced between 1971 and 1972 to investigate the hydrologic processes and radionuclide distributions in the cavity and chimney following the detonation. During the drilling operations, approximately 4000m<sup>3</sup> of radioactive gases, primarily consisting of krypton (<sup>85</sup>Kr), tritium (<sup>3</sup>H), and carbon (<sup>14</sup>C), were released to the atmosphere. Subsequent investigations indicated no evidence of surface deposition of these radionuclides. The water used to decontaminate equipment was injected into the well, and all tools, valves, and pipes suspected to have been contaminated were placed or cut and placed into the well cellar, and subsequently buried and sealed with 1.2m of concrete (Claassen 1978; Faller and Farmer, 1997; Dasher and others 2002).

### 5.4 POST TESTING ASSESSMENT

A review of site assessments, as they pertain specifically to the underground nuclear tests detonations, is included in the following. This review is limited to the assessments regarding the detonations, and does not include assessments of the impacts of other human activities and military occupations nor the site preparation and support activities related to the nuclear tests.

#### 5.4.1 *Initial post shot assessments: Long Shot*

Geological investigations conducted by the USGS from 1963 until shortly after the Milrow test are summarised by Carr and others (1971). No geological impacts associated with the Long Shot and Milrow tests were observed. However, the authors note that ‘a few minor slumps or rock falls occurred along the sea cliffs.’ An earlier report by McKeown and others (1967) reported more specific observations regarding the immediate observable effects of the Long Shot test. They noted fractured ground, mostly in unconsolidated ground, as far as 2255m (7400ft) away from surface ground zero (SGZ), tilted ponds, ponds and streams with slumped banks, and several mud geysers.

Following the Long Shot detonation, sampling revealed leakage of radioactive hydrogen (tritium  $^3\text{H}$ ), iodine ( $^{131}\text{I}$ ), and krypton ( $^{85}\text{Kr}$ ) to the surface and near surface environment, assumed to be attributable to the upward migration of radioactive gases due to expansion and displacement from cavity collapse and/or displacement due to groundwater infiltration. Initially,  $^{131}\text{I}$  was detected in a slump pond 100m from the Long Shot SGZ in November 1965. Tritium was detected in several slump ponds and drainage ditches in the vicinity of SGZ, and was monitored until May 1969 by contractors for AEC. A maximum tritium concentration of approximately 16,600 pCi/L was detected in a ditch 60m east of SGZ in September 1966. This concentration was higher than the background at that time, however, was less than the drinking water limit for tritium of 20,000 pCi/L (Castagnola 1969; Seymour and Nelson 1977; Faller and Farmer 1997; Dasher and others 2002; USDOE 2006).

#### 5.4.2 *Amchitka Bioenvironmental Program*

As a result of the status of Amchitka Island as part of a national wildlife refuge, the Amchitka Bioenvironmental Program was created by the AEC and administered through the Nevada Operations Office of the AEC, now known as the USDOE, in order to predict and mitigate the effects of the Milrow and Cannikin tests, to establish baseline information prior to the tests, and to document their impacts. The studies conducted under this programme began in 1967, following the Long Shot detonation, and ended in 1973 after the Cannikin detonation. The results are summarised in a series of papers published under the title, *The Environment of Amchitka, Alaska* (Merritt and Fuller 1977). The impacts to the environment of the Milrow and Cannikin tests are summarised in the following.



#### 5.4.2.1 Milrow

The Milrow detonation resulted directly in notable terrain changes. Rockfalls near the Amchitka coasts moving 6900m<sup>3</sup> of material occurred within 4km of SGZ. A fault shift caused an average 12cm (5in) uplift of approximately 4ha along an intertidal bench along the Pacific Ocean side of the island at Duck Cove. Tears and fractures in the peat mantle occurred surrounding SGZ and explosive disruption of natural tundra mounds were documented. Near SGZ, the collapse of the chimney caused tilting and fissure openings in the bottoms of two small lakes, which partially drained (Burkett 1977; Fuller and Kirkwood 1977).

These terrain and surface changes resulted in impacts to both the terrestrial and marine biota of Amchitka Island. The drainage of the small lakes resulted in impacts to the freshwater fish populations and biota. Pressure shock killed many threespine sticklebacks *Gasterosteus aculeatus* in those lakes, and some fish were thrown from the water during the blast. In the uplifted intertidal zone, massive algae and invertebrate kills were documented. It was generally thought that these impacts would not be permanent; however there was a permanent shift in the ecological system of the uplifted region. There were no observed impacts of Milrow on the bird populations of the island, nor on the marine fish or marine mammal populations, although weather prevented many of the planned monitoring activities following the blast. No evidence was found of radionuclides in marine, biota, or freshwater environmental samples following the test (Burkett 1977; Valdez and others 1977; White and others 1977; Lebednik and Palmisano 1977; Simenstad and others 1977; Seymour and Nelson 1977; Fuller and Kirkwood 1977).

#### 5.4.2.2 Cannikin

The Cannikin detonation caused rock and turf falls totalling 30,000m<sup>3</sup> of material along the Bering Sea coast and 5000 m<sup>3</sup> along the Pacific coast. These occurred along lines of an estimated 7.5km and 2km, respectively. Fault shifting was far more severe than that associated with the Milrow test. On the Bering Sea coast, near Sand Beach Cove, a 1.9km section of intertidal bench was uplifted between 25 and 107cm and additional 3km of bench was uplifted 18cm. Terrain disturbances, in the form of extensive surficial cracks, tears, and scarps, occurred at distances up to 2.5km from SGZ. Six small lakes and ponds, up to 1.2km from SGZ, were either completely or partially drained due to tilting and/or bottom fissuring. A large subsidence crater was formed during chimney collapse, covering an area of 12ha with a maximum depth of 9.45m. This crater

interrupted the flow of White Alice Creek, which filled the crater during 13 months following the Cannikin detonation, before normal flows resumed in the creek. This resulted in the formation of Cannikin Lake, which is the largest and deepest lake on Amchitka Island (Burkett 1977; Fuller and Kirkwood 1977).

There were massive fish kills of both marine and freshwater species associated with the Cannikin detonation. Within a 1.8km radius of SGZ, pressure shocks, stranding as a result of drainage, and explosive throwing from the water, killed approximately 10,000 threespine sticklebacks and 700 landlocked dolly varden *Salvelinus malma*. Populations recovered in all but the permanently drained surface waters. Stranding on uplifted intertidal benches and/or shock waves killed 300 rock greenling *Hexagrammos lagocephalus*, and rock sole and rock greenling catches were observed to have been impacted for a period of approximately 1 year after the test. Rapid pressure changes and rock falls killed 12 sea otters and 4 harbour seals that were recovered following testing. It was estimated that several hundred sea otters were killed by the test; no estimated kills on seal populations were ever made. Massive algae and invertebrate kills were observed in the uplifted intertidal benches, and permanent shifts in the ecological communities resulted from the vertical displacements. Fifteen birds were found killed from pressure shock in the water and/or vertical acceleration on land, and it was estimated that many more were actually impacted. Several bald eagle nests and peregrine falcon eyries were destroyed and/or damaged by the test, though it was estimated that this damage would not have long term consequences (Burkett 1977; Valdez and others 1977; White and others 1977; Lebednik and Palmisano 1977; Simenstad and others 1977; Seymour and Nelson, 1977; Fuller and Kirkwood 1977).

#### 5.4.3 Long term hydrological monitoring

The USGS installed several shallow groundwater wells in 1971 following the documented tritium release to the surface associated with the Long Shot test. The United States Environmental Protection Agency (EPA) began a sampling these wells and analysing for tritium and gamma-ray emitters in 1977 and lasting until 1997 as part of the Long term hydrological monitoring programme. No gamma ray emitters were detected, and tritium was found in the vicinity of Long Shot SGZ, with the zone of maximum contamination between 60 to 100m (200 and 300ft). During the years of monitoring, tritium concentrations were decreasing, due to decay and dilution (Faller and Farmer 1997).

#### 5.4.4 *Investigations of potential surface leakage of radionuclides*

In 1996, Greenpeace collected samples of aquatic biota from Amchitka Island with the aim of investigating the potential surface release of radionuclides. In 1996, Miller and Buske reported that the samples indicated the release of americium-241 ( $^{241}\text{Am}$ ) and plutonium-239+240 ( $^{239+240}\text{Pu}$ ) in the vicinity of the Cannikin test shot. In 1998, Buske and Miller (1998) reported on additional analyses and indicated the potential release of  $^{241}\text{Am}$  from the Long Shot, Milrow, and Cannikin test shots.

As a result of the 1996 report, sampling excursions occurred in 1997 and 1998 jointly by the US EPA, USDOE, Alaska Department of Environmental Conservation (ADEC), the Aleutian and Pribilof Islands Association (APIA), Greenpeace, and the University of Alaska Fairbanks. These sampling efforts included water, vegetation (freshwater moss and marine algae), lichen, soils, sediments, and freshwater fish both from the watersheds of the three test shots as well as control samples. The samples were analysed for tritium, gamma and alpha emitters, and the ratio plutonium-240/plutonium-239 ( $^{240}\text{Pu}/^{239}\text{Pu}$ ), which can be compared to global fallout and regional means for the latitude. The investigations did not indicate any release of tritium, radioactive americium, nor other radionuclides from the test cavities to the surface terrestrial or freshwater environments, other than those associated with the documented release of tritium from the Long Shot test (Dasher and others 2002; USDOE 2006).

#### 5.4.5 *Groundwater modeling*

The conceptual model for the transport of radionuclides released in the subsurface by the detonations to the surface environment is illustrated in Figure 5.3. In this model, mobile radionuclides, if present, would be transported with groundwater flow from the test cavities to the ocean floor. The results of early predictive groundwater modeling and radionuclide transport for the Cannikin test shot were reported by Fenske (1972). The model predicted that groundwater from the Cannikin shot chimney should be transported to the Bering Sea ocean floor with an average groundwater travel time of more than 3000 years, where the model assumed dilution and mixing in the ocean following seepage to the sea floor. A later model by Wheatcraft (1995), determined a travel time for water from the Long Shot cavity to the ocean floor of between 800 and 1700 years, depending largely on the location of the freshwater/saltwater transition zone, a region characterised by an increasing salinity with depth. The model considered a spatially and temporally constant recharge and a single hydraulic conductivity for an isotropic, homogeneous

subsurface. Wheatcraft suggested that the model could be improved by consideration of a layered geologic system.

Hassan and others (2002) modeled the radionuclide transport to determine travel times and potential seepage locations from all three test shots in an effort to improve risk assessments. Their models were two dimensional and included extensive uncertainty analyses using Monte Carlo techniques. The uncertainties considered included: hydraulic conductivity, recharge, fracture porosity, dispersivity, as well as less detailed analyses regarding uncertainties in heat driven flow and three dimensional considerations. The models considered a homogeneous hydraulic conductivity with a range of values. Analyses of the results indicated that the shortest peak arrival time to seepage locations from the test cavities for tritium of 20 to 30 years for Long Shot and 100 to 125 years for Milrow and Cannikin. The shorter travel time associated with Long Shot resulted from estimates that placed the Long Shot detonation above the freshwater/saltwater transition zone, while the Milrow and Cannikin detonations were assumed to have occurred in the transition zone. The mass breakthrough times for test related radionuclides were over 2,200 years for nearly all of the Monte Carlo realisations at the three test sites. The model was determined to be highly sensitive to fracture porosity, diffusion of radionuclides into the matrix rock, and uncertainties in the locations of the transition zones for the three test locations.

The Consortium for Risk Assessment with Stakeholder Participation (CRESP) began investigations aimed at addressing these and other uncertainties regarding the transport of, and health risks associated with, the radionuclides in the subsurface at Amchitka Island in 2002. As part of the CRESP investigations, magnetotelluric (MT) surveys were performed across transects intersecting each of the three test sites in 2004. The results of the MT surveys resulted in improved estimates of the depths to the transition zone and the variation of effective porosity with depth. The MT survey indicates that all three of the test shots were located in the transition zone. Unsworth and others (2007), report an effective porosity of 10–20% at the ground surface, decreasing with depth to 1–3% at 3000m below ground. These authors indicated that the location of the test shots in the transition zone, as opposed to the saltwater zone, would result in shorter path lengths to the ocean floor, hence reducing travel times. However, the higher porosities determined by MT would result in longer ultimate travel times (Powers and others 2005; Unsworth and others 2007). It is noted, however, that the large scale of the MT measurements

(3km depth) allows large scale interpretations of effective porosities in the subsurface, however, the results of MT investigations cannot be applied to interpret fluctuations in porosities which will occur with geologic layers in the subsurface rock.

As part of the CRESP science studies, groundwater modeling with improved data on the transition zone depths and bathymetry were performed for the Long Shot test site (Powers and others 2005) and the Cannikin site (Wagner 2007). Various simulations performed in these analyses included consideration of isotropic subsurface, anisotropic subsurface at ratios of 1:2 and 1:10, longitudinal dispersivity, and varying rates of recharge to the island from precipitation. No retardation effects on radionuclide transport due to diffusion and sorption of radionuclides into matrix rock or decay were considered. Groundwater travel times at the Long Shot site from the test cavity to the ocean floor ranged from 1,400 to 4,700 years for the various scenarios considered. However, previous investigations indicate that the Long Shot detonation occurred in an andesite sill, a geological unit characterised by a high hydraulic conductivity due to an extensive fracture network. When the influence of the andesite sill was considered in the model, the groundwater travel time ranged from 400 to 1,400 years. Groundwater travel times at the Cannikin location from test cavity to ocean floor ranged from 2,100 to 4 million years. While these estimates of groundwater flow are similar to the 2002 model, Wagner (2007) notes that this commonality is the effect of different considerations of effective porosity and anisotropy. The 2002 model considers a low porosity as compared to the 2007 model, which leads to shorter transport times, while the 2002 model also considers a higher anisotropy, which leads to longer transport times as compared to the 2007 model. Therefore, further investigations to reduce these uncertainties were recommended (Wagner 2007).

Diffusion coefficients and porosities of samples of rock from pre-shot exploratory cores, most in the vicinity of the Cannikin test shot, have been measured in laboratory experiments by the authors (Benning 2008). The results of the experiments indicate that on a finer scale than indicated by MT investigations, porosities vary significantly with geologic layers from approximately 9% for andesites, to 12–14% for basalts, to 13–29% for breccias, with low porosity layers interspersed with high porosity layers throughout the depth of a core. The diffusion coefficients correspondingly range by more than two orders of magnitude for the low and high porosity samples. These results indicate that, as suggested by Wheatcraft (1995), a layered subsurface system is a more likely scenario for modeling the transport of radionuclides

through Amchitka Island's subsurface. The andesite sill layer at the Long Shot test site modeled by Wagner (2007) indicates that this layer represents a potential preferential flow path due to its extensive fracture network, and when this layer is considered, short groundwater travel times from test cavity to ocean floor result. The low porosity and low diffusion coefficient for andesite indicates that there would be relatively little retardation and storage of radionuclides in this layer, and thus radionuclide travel times in this layer would be much closer to groundwater travel times.

Hassan and Chapman (2006) revised their 2002 statistical groundwater model using data derived in the CRESPP studies to reduce uncertainties in the model. The 2006 model incorporated the results of the MT surveys regarding the depths of the transition zones and effective porosities at the three sites, as well as bathymetric data summarised in Powers and others (2005). The additional data was determined to have dramatically reduced uncertainties in the 2002 model. The groundwater velocities were decreased by approximately an order of magnitude, as a result of the increased effective porosity provided by the MT surveys; and for all realisations, the travel times were greater than the 2,200 year modeled time scale.

#### *5.4.6 Screening risk assessment*

The USDOE prepared a draft screening risk assessment report in 2005 as part of the site investigations of the long term management of the site. However, the ADEC and APIA did not accept the results of this assessment, and instead requested that USDOE efforts should focus on the development of the long term management plan. As stated in the later USDOE report (USDOE 2008: 3–17): ‘ADEC and the Stakeholder group have serious concerns regarding the human health risk assessment and lack of ecological risk assessment. If discussion of the risk assessment is included, a clear statement should precede these sections stating that ADEC and the Alaska Stakeholder group do not concur or approve of the risk assessment.’

#### *5.4.7 Amchitka independent science assessment*

The CRESPP science plan for Amchitka Island was developed through active participation and collaboration of the major stakeholder parties for the island through all stages of planning and research (Burger and others 2005). The development of a conceptual site model was a necessary step to defining the problem and identifying the potential receptors and stakeholders (Burger and others 2006a). The major stakeholders concerned with the potential release of radionuclides to the environment from the Amchitka underground nuclear tests include: the Aleutian Pribilof

Islands Association (APIA), the Alaska Department of Environmental Conservation (ADEC), US Fish and Wildlife Service (USFWS), and the US Department of Energy (DOE). The major objectives of the science plan were to assess the current safety of consumption of subsistence and commercial food sources derived from the environment surrounding Amchitka, to provide baseline data and to promote scientific studies to reduce the level of uncertainties in the transport modeling and risk assessment of radionuclides released underground at Amchitka (Burger and others 2005; Burger and others 2007a). The results of the execution of the science plan are summarised in the 2005 report entitled 'Amchitka independent science assessment' (Powers and others 2005). The results of some of the physical assessments are summarised in the preceding section, and the biological components are summarised in the following and described in several papers (Burger and others 2006b, c, 2007a-d).

Since the major concern of several stakeholders was the potential for radionuclide contamination of biota in the marine environment surrounding Amchitka, CRESPI researchers held several meetings in the Aleut villages and with other natural resource trustees. These meetings served to identify the species that stakeholders were most concerned about, to seek additional input concerning other biota to sample, and to solicit any other views about the sampling plan. These meetings resulted in changes to the initial sampling plan, as well as the inclusion of Aleuts on the expedition to collect samples in their traditional manner (Burger and others, 2007a,b).

The sampling plan included collecting specimens from the marine environment around the three Amchitka test shots and at a reference site (Kiska Island). Specimens collected in summer of 2004 included in marine biota representative of different trophic levels (kelp, invertebrates, fish, birds) and subsistence and commercial foods. One important aspect of the sampling plan was that several different species were collected at each trophic level to ensure that radionuclide bioaccumulators were included. The inclusion of Aleuts as participants in the sample collection ensured that some biota were collected in the traditional manner from typical fishing and hunting locations. Their inclusion also allowed the expedition to add traditional foods not previously included in the initial sampling plan. Further, the Aleut researchers could report the results back to their villages from first-hand experience.

Salinity measurements of the ocean floor conducted under this programme indicated that there was no major freshwater discharge, which would occur if there were preferential flow from the

island's subsurface to the ocean floor through faults, and hence no major preferential pathway for radionuclide transport was detected. The studies, however, also revealed regions of ocean floor adjacent to the Cannikin and Long Shot test locations with large sediment accumulations. These deposits, which in previous risk assessments had been assumed to not exist, have potential to accumulate radionuclides, if there were seepage from the subsurface, whereupon there would be potential to enter the food chain via accumulation of exposed sedentary biota such as kelp (Powers and others 2005).

The results of the 2004 sample analyses and risk evaluations indicated that there was no current risk from radionuclides to humans or environmental receptors from the underground testing at Amchitka Island (Burger and others 2007c-e). None of the biota sampled in 2004 displayed any detectable amounts of iodine-129, cobalt-60, europium-152, strontium-90, or technetium-99. Some samples contained trace amounts of americium-241, uranium-236, plutonium-239 and -240, and cesium-137; and nearly all samples contained uranium-234, -235, and -238. Comparison of Amchitka Island samples to samples collected from the reference island, Kiska, and other global reference locations did not indicate that the presence of these radionuclides could be associated with the Amchitka Island nuclear tests. However, the analyses indicated that plutonium and uranium tended to concentrate in algae, kelp, and filter feeders, such as rock jingles *Pododesmus macroschisma*, while the marine fish, especially those on higher trophic levels tended to concentrate caesium. Thus, CRESP recommended that the long term stewardship plan should include monitoring of both sedentary and mobile biota that represent different levels on the food chain, commercial fish, and subsistence species (Burger 2007).

The results of the radionuclide analyses of the full suite of biota also provided data to assess the current risk to commercial and subsistence foods. However, further radionuclide analyses were required to provide enough data to identify the biota at each trophic level that were the greatest accumulators of radionuclides, since these would provide the earliest warning of any potential problems (Burger and others 2007f). CRESP recommended two species of kelp, *Fucus* and *Alaria fistulosa*, a filter feeder invertebrate (blue mussel *Mytilus edulis*), dolly varden as a commercial and subsistence fish that is anadromous, black rockfish *Sebastes meanops* because of its subsistence value, pacific cod and halibut as top level fish predators of subsistence and commercial value, and glaucous-winged gull (*Larus glaucescens*) because it is local, long-lived, and the eggs are a subsistence food (Powers and others 2006, Burger and others 2007f). This



combination of species represents key trophic levels, as well as commercial and subsistence foods.

## 5.5 LONG TERM STEWARDSHIP

At many USDOE sites throughout the United States, technological and economic limitations prevent cleanup activities from achieving a state that would allow unrestricted access and use of the site in a manner that would still ensure the health and safety of current and future generations. For some sites, particularly those that are a legacy of the USDOE nuclear weapons programmes, the nature of the contaminants themselves inhibits feasibility of remediation. Many radionuclides, for example, have very long half lives and thus are very persistent in the environment; furthermore, many decay into radioactive daughter products that also pose health hazards. For these sites, the USDOE implements ‘long term stewardship’ or ‘long term management’, a plan of actions designed to minimise current and future human health risks associated with remaining (residual) contamination at these sites (USDOE 1999; USDOE 2001).

The term ‘stewardship’ is defined by the USDOE as ‘activities necessary to maintain long-term protection of human health and the environment from hazards posed by residual radioactivity and chemically hazardous materials’ (STGWG 1999). In practice, this entails all of the activities required to ensure the protection of human health and the environment for a site after remediation is ‘complete’, economically and technically feasible options for remediation are exhausted, or further remedial options would present increases in risks to human health (USDOE 1999). Several groups provide information and recommendations as to how long term stewardship should be handled at these sites, such as the USDOE (USDOE 1999; USDOE 2001), the National Research Council (NRC) (NRC 2000), and the State and Tribal Government Working Group (STGWG) (STGWG 1999). Others provide additional discussions and recommendations regarding long term stewardship as well, such as Burger (2000), Burger (2001), and Burger and Gochfeld (2001).

At Amchitka Island, USDOE has conducted surface cleanup to a level acceptable to the ADEC. However, since there are no available technologies to remediate the radionuclides released from the underground detonations and remaining in the deep subsurface of the island, the USDOE has transferred the site from a state of active remedial management to long term stewardship.

### 5.5.1 *Long term surveillance and maintenance plan for Amchitka Island*

The USDOE published their plans for the long term stewardship at Amchitka Island in February 2008, in a report titled ‘Long-term surveillance and maintenance plan for the U.S. Department of Energy Amchitka, Alaska, Site’ (LTSMP). The stated objectives of the LTSMP are: to collect data and report data to verify that human and ecological health is protected, to maintain site records for future generations, to plan for contingencies, and to provide a venue for stakeholder and regulator involvement (USDOE 2008).

The LTSMP employs institutional controls and monitoring to ensure the protection of human and environmental health in association with the risks posed by the radionuclides released to the subsurface in the underground testing on Amchitka. The institutional controls include: warnings to all potential visitors to the island of the radionuclides and appropriate access restrictions to be administered through USDOE, USFWS, and the National Oceanic and Atmospheric Administration (NOAA); specific restrictions against activities that would cause surface disturbances in restricted areas and/or ground penetration; future deed restrictions, if necessary, on pending native claims on the island, if awarded; the maintenance of monuments at the surface ground zeros of each of the three test sites, Long Shot, Milrow, and Cannikin; and the maintenance of surface covers on the previously closed drilling mud pits. USDOE intends to conduct site inspections at 5 year intervals to ensure the continued protection of these control measures (USDOE 2008).

Since the main pathways of concern for radionuclides from the subsurface to the surface environment, as identified by the previously discussed assessments for Amchitka Island, are through groundwater discharge to the marine environment, the continued monitoring of the marine environment and biota is deemed sufficient to identify potential releases and their associated health risks (Powers and others 2005; USDOE 2008). Essentially following the recommendations provided by CRESP (Powers and others 2005; Powers and others 2006), the USDOE plans to sample and monitor the following species on 5-year intervals: cod, dolly varden, greenling (kelp or rock), halibut, rockfish (black or dusky), sea urchin, mussels, gumboot chitons *Cryptochiton stelleri*, gull eggs, and kelp (*Fucus* and *Alaria fistulosa*). The kelp species are included because these are high bioaccumulators of plutonium, uranium, and americium isotopes and are good bioindicators for early warnings. Specifically, halibut is noted for its importance as a commercial and subsistence food source, and glaucous winged gull eggs are of importance in

the traditional Aleut diet. These samples will be analysed for: cesium-137, americium-241, plutonium-239 and -240, total uranium, gross alpha emitters, gross beta emitters, and gross gamma emitters, though it is noted that only the gross alpha, beta, and gamma will be included for analyses following the initial two sampling events, after which, the individual radioisotopes will be dropped from the analyses. Additionally, USDOE plans to sample seawater and analyse for tritium, as the most mobile radionuclide, at 5 year intervals (USDOE 2008).

The LTSMP includes review and re-evaluation of the plan at 5 year intervals. The availability of data and reports to the public and stakeholders is limited to 'selected site documents', to be accessed either by the Office of Legacy Management's (LM) website, [www.lm.doe.gov](http://www.lm.doe.gov), in libraries, such as the regional APIA library or the University of Alaska Anchorage Consortium Library, and at the USDOE Office of Legacy Management in Grand Junction, Colorado. The plan also details planning for participation and oversight of the site by ADEC, USFWS, and APIA through participation in routine site inspections and monitoring events, review of documents, and consultation regarding 5 year reviews and contingency planning. The plan furthermore includes a list of contacts of governmental officials and key stakeholder and community group leaders, all who are to be 'kept informed of site activities and status changes'. USDOE's commitment to public awareness and involvement is discussed in the LTSMP, and includes: providing information and documents through the LM website; holding public meetings, as needed; and holding briefings with APIA and state and local officials, as needed (USDOE 2008).

Contingency planning is detailed in the LTSMP. As there is specific concern over the potential for catastrophic events at Amchitka Island, since the region is known for its high level of tectonic activity and frequency of large magnitude earthquakes, the USDOE plans to review plans and potentially increase monitoring following any earthquakes of more than 6.7 magnitude at Amchitka Island or within its vicinity. ADEC, USFWS, and APIA will be included in the review and planning following such an event. Volcanic activity, significant shifts along faults, and subduction-influenced movement on the island will be considered. USDOE indicates that it has plans to develop an 'emergency response plan for the island' (USDOE 2008).

In the event of the detection of radioisotopes above the acceptable levels for ingestion during the routine monitoring, the USDOE plans to consult ADEC, APIA, and USFWS on actions necessary

for the protection of human health. It is noted that possible actions listed include the issuance of public warnings or temporary catch restrictions (USDOE 2008).

#### *5.5.2 Uncertainties at Amchitka and their implications*

There remain significant technological and scientific issues of uncertainty, which could have important implications to the long term fate and transport of radionuclides from the subsurface at Amchitka Island. One of these key uncertainties is the potential for catastrophic events, such as large magnitude earthquakes, to open new pathways for radionuclides from the subsurface to the surface, or marine, environment. Current scientific knowledge limits any understanding of the potential for such an occurrence, and therefore, the re-evaluation and possible monitoring following an earthquake over 6.7 magnitude, as recommended by USDOE, is considered the only appropriate and feasible means of ensuring public health in association with such an event. In addition to concerns of catastrophic events, however, there is also concern over the potential impacts to the transport of radionuclides resulting from the island's movement (Attu Island, for example has been shown to be moving relative to mainland North America at a rate of 3 cm/yr as noted by Eichelberger and others 2002). Continued research into this issue has been recommended by APIA, as this uncertainty remains a significant concern to stakeholders (Pletnikoff 2008).

The groundwater models, and associated estimates of the transport of radionuclides through the subsurface environment, though significantly improved with regards to their uncertainties with the input of the results of the CRESP studies, still also remain as significantly uncertain. While the 5 year monitoring interval should be sufficiently protective to ensure public health against earlier breakthrough than is predicted by the groundwater models, it is still important to highlight and emphasise this as an uncertainty, particularly in light of the significant failures of groundwater models at other USDOE legacy sites. The NRC report (2000) cites the examples of the Idaho National Engineering Lab (INEL) and the Nevada Test Site (NTS) where the transport of radionuclides in the subsurface has been shown to be dramatically faster than had been predicted in models, demonstrating the consequences of relying on simplified fate and transport models for complex, multi-scalar, heterogeneous subsurface conditions and the need for further research.

At Amchitka Island, in particular, it is noted that the CRESP model that included consideration of preferential flow through the highly fractured andesite sill located at the depth of the Long Shot detonation resulted in significantly shorter travel times, 400 to 1,400 years (Powers and others 2005), as opposed to travel times greater than a 2,200 year model time in other conceptualisations (Hassan and Chapman 2006). In addition to the potential impacts of increased flow through this sill layer, estimates on the diffusion into matrix rock in andesite indicate the probability of little retardation in this layer (Benning 2008). Furthermore, uncertainties in the actual fracture porosities still exist, which is of concern since modeling has shown that the simulated travel time is very sensitive to this parameter. Thus, the estimated travel times are significantly increased or decreased when the porosity changes by a few percent, making the prediction of the exact radionuclide arrival times difficult. Data on the porosity and diffusion characteristics of the subsurface materials at the Cannikin location indicate a highly variable and structurally layered subsurface (Benning 2008), which has not been included in groundwater modeling approaches to date. In the LTSMP, while it acknowledged the existence of the much shorter travel time indicated in the CRESP groundwater model, preference is given to the later modeling by Hassan and Chapman (2006) that indicated a much greater travel time. APIA also expresses concerns over the uncertainty of the groundwater model, stating that the models must be 'accurate, properly interpreted, and must be verifiable.' They furthermore recommend that additional porosity and transport studies are warranted for Amchitka Island, given the sensitivity of the modeled travel time to porosity (Pletnikoff 2008). The open acknowledgement of this uncertainty and continued efforts and investments to reduce the uncertainty are key issues that need to be addressed, as recommended by the NRC (2000).

The uncertainties surrounding the groundwater models result in uncertainties in the determination of the appropriate biomonitoring interval. That is, the time for transport of radionuclides to the marine environment, either through natural processes or catastrophic geologic events or disruptions, is difficult to predict. Further, once radionuclides reach the marine environment, there are several biological uncertainties, including 1) biotic species composition at the site of any seepage, 2) complexity of the food chain at the location of any seepage, 3) time to move up the food chain at the site of the seepage, 4) mobility of each species, and 5) the timing of any seepage (seasonality) will influence the composition and abundance of biota at any marine location. That is, any seepage during the summer could result in more rapid transport up the food chain than

would occur in the winter. Further, the location of any seepage (and thus the depth of water at that location) will affect all of the aforementioned uncertainties. There are also some analytical uncertainties involved with the lower precision of values when radionuclide levels are close to detection levels.

An additional and important uncertainty is how often and how much of the marine foods are collected by commercial fisheries and subsistence users. This value varies with conditions; in 2005, the halibut fishing was depressed near many of the Aleut villages and their fishermen went as far as Amchitka to meet their quotas (Burger and others 2007g). The relative use of the marine environment around Amchitka becomes even more important if there is any seepage because an exclusion zone would have to be created to protect human consumers. While there is currently no discernible risk to humans from radionuclides released from the underground tests at Amchitka, the purpose of future biomonitoring is to provide early warning.

## 5.6 CONCLUSIONS

Consideration of the long term management of remote sites, such as Amchitka Island, where the hazards remaining will persist far into the future is complex and difficult. And for Amchitka Island, there is no available technology to remediate or isolate the radionuclides released in the subsurface during the detonation of the three underground nuclear tests conducted there. The long term stewardship and management of the site is essential in order to protect the health of future generations and the environment. The USDOE plans to manage the site through a combination of institutional controls, routine monitoring of marine biota, and contingency planning, as detailed in their LTSMP.

While this management plan is deemed to be essentially protective of human and ecological health over the long term, several deficiencies are noted. Catastrophic events will remain a potential hazard, and to address this potential, the DOE plans to develop an 'emergency response plan'. The LTSMP includes discussion of groundwater models, but does not openly acknowledge the level of uncertainty involved in these models, and does not commit agencies to support research and development to improve scientific and technical knowledge regarding these uncertainties for Amchitka Island. Additionally, there is no noted discussion or commitment provided in the LTSMP that would address the remaining biological uncertainties. Furthermore, the LTSMP indicates that review of the plan will be conducted on 5 year intervals; however, no

explicit commitment is made to review technological and scientific advances made during those time periods outside of or within the context of USDOE legacy sites.

Though one of the primary objectives of the LTSMP is to ‘provide a mechanism for stakeholder and regulator involvement’ and USDOE’s recommendations on long term stewardship indicate the importance of public education in the sustainability of long term plans, the provisions for these in the LTSMP are highly ambiguous. Public and stewardship meetings, according to the plan, will be held ‘as needed’, rather than explicitly stating plans for public involvement, awareness, and education. The inherent fallibility of long term institutional management, as detailed by NRC (2000), indicates that this level of ambiguity will probably lead to the failure of this measure.

In conclusion, consideration of the long term management and stewardship of Amchitka Island needs to emphasise that, although the island is perceived as remote and uninhabited, this perceived ‘remoteness’ should be viewed in light of its significant importance to both subsistence (according to Pletnikoff 2008, 66% of the diet at Atka is subsistence food and 100% of Aleut households use subsistence foods) and commercial food supplies. Its ‘uninhabited’ status should be considered in the context of the relatively recent history that yielded that status. Furthermore, owing to the historical occupation of the island, it cannot be assumed that the population statistics of the western Aleutians will remain constant in the future.

## 5.7 RECOMMENDATIONS

In order to address some of the remaining concerns and uncertainties at Amchitka Island, we recommend, in addition to the LTSMP, the formation of a technical advisory panel. It is the opinion of the authors that this panel should include representatives from the DOE, the State of Alaska, the USFWS, and the Aleutian community, as well as technical experts in marine biology, contaminant hydrology, and geology/seismology. It is proposed that this board should meet twice every five years, once a year after each monitoring event to review recent data, and again two years after that to provide recommendations for the subsequent monitoring event. The technical advisory board would be responsible for the review of current literature regarding recent scientific and technical developments and would direct additional research for the site specifically, as necessary. This board would also provide support in the dissemination of

information to the public and stakeholders, and would be qualified to organise and direct public education.



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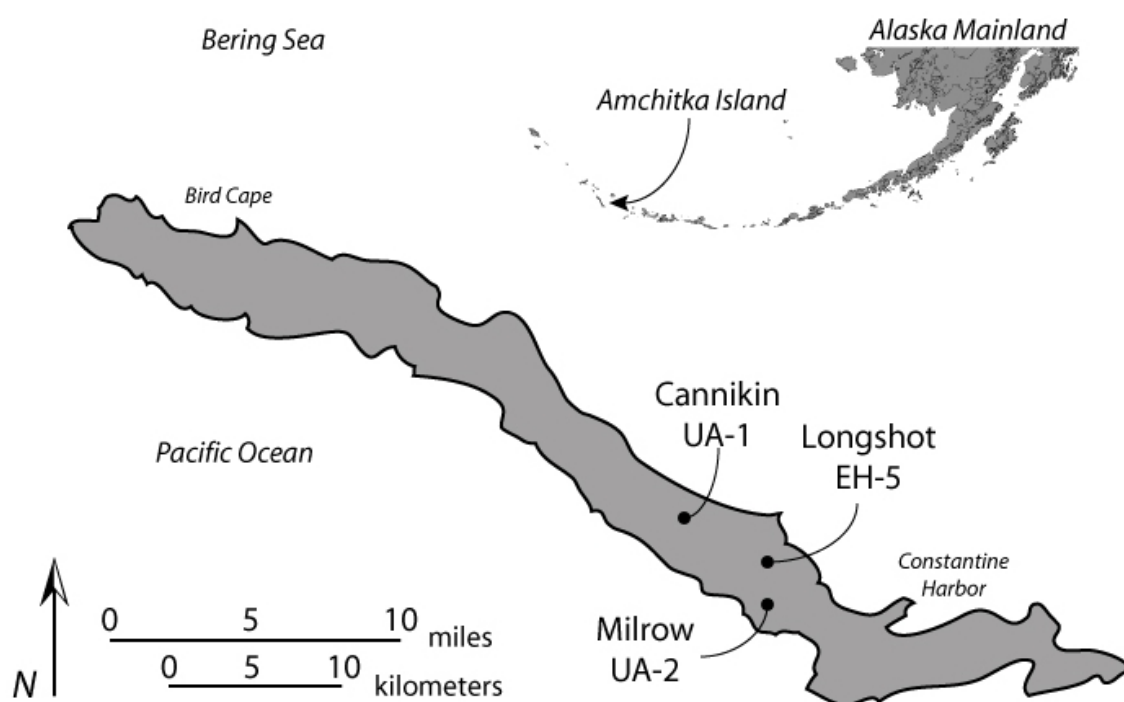
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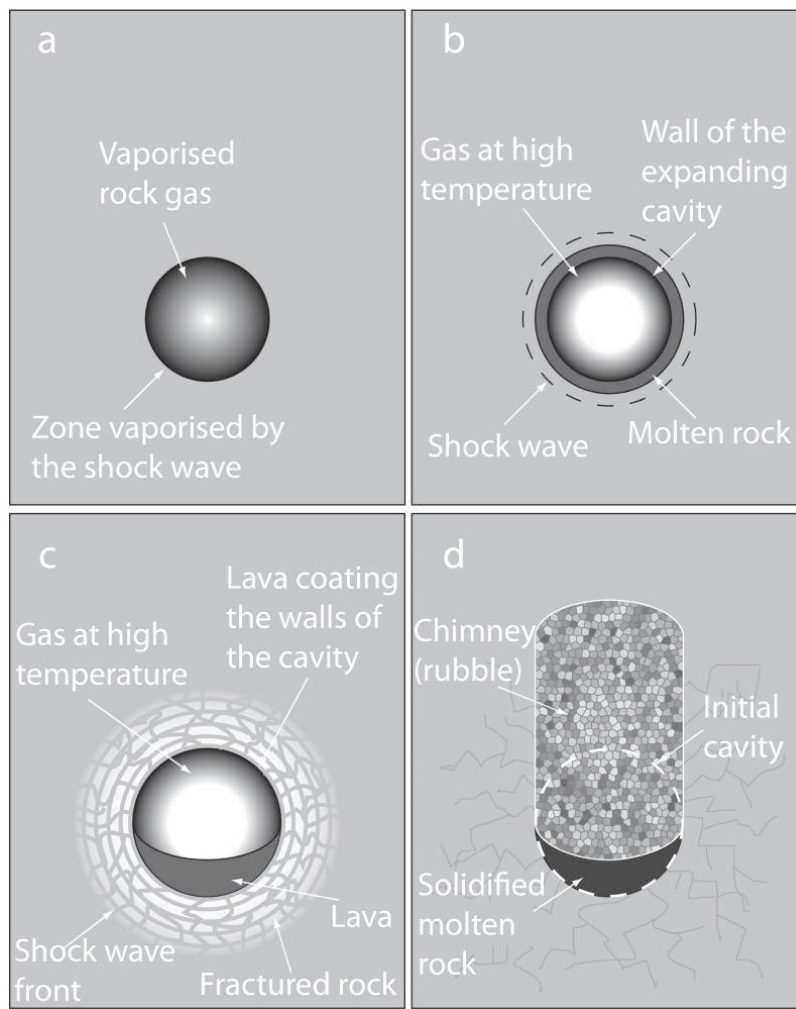
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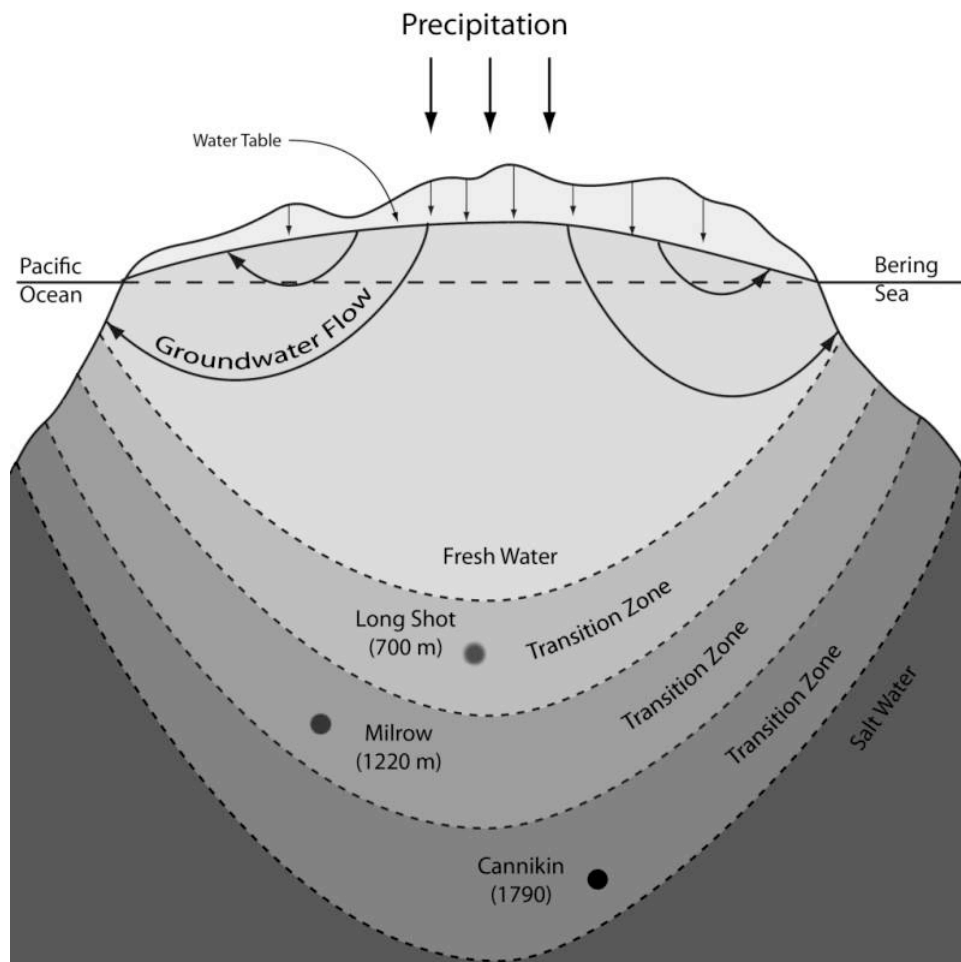


**Figure 5.1** Map of Amchitka Island, Alaska showing the location of the three underground nuclear tests: Long Shot, Milrow and Cannikin.





**Figure 5.2** Illustration of the phases of an underground nuclear detonation (a) after tens of microseconds, (b) after hundreds of microseconds, (c) after tens of milliseconds, (d) after minutes to hours. Adapted from IAEA 1998b.



**Figure 5.3 Conceptual model of the Amchitka Island hydrology.** It is noted that the depth of the transition zone varies widely amongst the three test sites. For a more detailed discussion of island groundwater hydrology, see Fetter, 2001

## 5.10 APPENDIX



## 6 CONCLUSIONS

The objectives of this study were to investigate the effects of scale and pore system connectivity on the intrinsic diffusion coefficient for volcanic matrix rock and to investigate the impacts of spatial heterogeneities, particularly in regards to highly heterogeneous breccias, on intrinsic diffusion coefficients. Since the results of these studies are important to the understanding of radionuclide transport through the subsurface at Amchitka Island, an associated objective of this study was to assess the range of diffusivities found in the different rock types that comprise the subsurface of the island. Recommendations for radionuclide transport modeling are made in light of these effects. A final objective was to apply the knowledge gained through these investigations to an analysis of the long-term stewardship plan for Amchitka Island and to provide recommendations for improvement of the plan.

In order to provide a basis for the studies into the effects of scale and spatial heterogeneities on the diffusive transport of contaminants, an investigation was made into the methods of solution for the through-diffusion test. The through-diffusion experiment is commonly used in laboratory studies to estimate the diffusion coefficients (diffusivity) and the effective porosity of porous media. However, it has been widely recognized that the derived estimates of the effective porosities are subjective and unreliable; this discrepancy arises from the method of solution to Fick's Law of diffusion to analyze transient-state experimental data.

Several different solutions to Fick's Law of diffusion and their applicability to the analysis of through-diffusion experimental data were examined using data from three experiments representing porous media with order of magnitude differences in their diffusivities. The results of the investigations indicated that there is relatively little difference in the intrinsic diffusion coefficient derived using the various through-diffusion solution methods even with a 4% change in the source cell concentration, which is a violation of the boundary conditions for the time-lag and approximate analytical methods. However, for applications in which the effective, or transport, porosity is significantly different from the bulk porosity, the use of a semi-analytical model, such as that developed by Moridis (1998, 1999), is required for the analysis of transient-state through-diffusion experimental data. And thus, in further studies designed to quantify the contributions of the various causes of the differences between the effective porosity and the bulk porosity (i.e. unconnected pores versus diffuse double layer and/or anion exclusion effects), the

application of a solution such as the semi-analytical method is essential, as it provides a substantial improvement to the derivation of effective porosity as compared to the commonly applied time-lag solution.

A further important conclusion resulting from the investigations of the solution methods for the through-diffusion experiments, was that it was observed that not all of the pore spaces in a natural porous medium may be connected and/or available for diffusion. This effect can be seen by comparison of the results of the natural samples, i.e. Core 19 and Core 24, for which the effective porosities are less than the bulk measured porosity, to the results of the porous plate sample, which was manufactured to have a well-connected pore structure. In confirmation of the results of Reimus, *et al.* (2007), this fact may have an important implication on the appropriateness of the scale of the sample measured in through-diffusion experiments. As seen in the Core 24 sample, for example, the derived effective porosity is likely not representative of measurements on a larger scale because the use of a thin slice allows pores to be connected that would otherwise be unconnected at a larger scale.

This knowledge was then applied to studies designed to understand the impacts of scale and spatial heterogeneities on diffusion at the study site. Multiple Amchitka Island core samples, both from the same and from various geologic layers, in varying sizes were analyzed in the laboratory via tracer-based and electrical methods, to quantify the diffusive properties and the effects of heterogeneities for Amchitka Island. The investigations indicate that there is some effect of scale on measured intrinsic diffusion coefficients and formation factors, but these effects are generally small in comparison to variability between lithologic layers. These effects are also generally limited to approximately 6 cm for most samples and are well-correlated with observed heterogeneous features. Similar to the results of Löfgren and Neretnieks (2006) for granites, the pore structures of the breccias and basalts present in the subsurface at Amchitka Island appear to be well-connected at the scale of laboratory measurements (up to 42 cm in length). For most of the samples investigated, the average formation factor for adjacent 1-cm sections of rock is approximately equal to the asymptotic value of the formation factor for increasing sample lengths, thereby implying that an adequate estimate for even the most heterogeneous of the breccia samples can be obtained either by conducting tests on multiple small samples or by conducting tests on longer samples, which allows for flexibility in experimental design. An

important conclusion resulting from this study is that there is a potential for the estimated formation factor to be misrepresented by an order of magnitude if multiple samples are not tested.

For individual geologic layers, the investigations indicate that the probability distribution function of the formation factor is normal, except when the sample is influenced by features with different properties than the surrounding matrix properties (e.g., an unconnected and unweathered fracture). However, the probability distribution function for the formation factor throughout the depth of the Cannikin vicinity subsurface shows a lognormal distribution, due to the order of magnitude differences between lithologic layers. The large skewness of the distribution is corroborated by the high  $m$ -factor in Archie's Law for the relationship between the porosity and formation factor for the Amchitka Island samples. An understanding of the probability distribution function is essential to stochastic modeling efforts.

The intrinsic diffusion coefficients and formation factors derived in these studies are much lower than those derived in previous, more limited diffusion studies for Amchitka Island. The formation factor and porosity profiles for the Cannikin test site show a strongly layered subsurface with a large spatial variability found in both parameters. The results of these investigations are anticipated to reduce some of the uncertainties associated with the radionuclide transport modeling at the island. The studies furthermore indicated that the diffusivities and porosities for the Amchitka Island rock varied widely, by greater than two orders of magnitude and more than 15%, respectively, thus indicating a strongly layered subsurface. Of particular concern for transport at Amchitka Island was the very low porosity and diffusivity of the andesite matrix rock, which is the media at the depth of the Long Shot test. These low values indicate a very low potential for retardation in this geologic media, while studies by Wagner (2007) indicated that layer as a preferential flow path for groundwater, due to its extensive fracture network. When the andesite sill layer at the Long Shot location was considered, the estimated travel time for groundwater breakthrough to the ocean floor was the shortest, an estimated 400 to 1400 years. If the impact of this shorter travel time is combined with the effect of the low potential for retardation, there is a concern that the radionuclides would not be significantly lowered from the groundwater transport rates, and the radionuclide travel could be significantly faster than predicted in other modeling efforts (Hassan & Chapman, 2006).

The results of the experimental investigations were applied to the question of long-term stewardship for Amchitka Island. Consideration of the long term management of remote sites, such as Amchitka Island, where the hazards remaining will persist far into the future is complex and difficult. And for Amchitka Island, there is no available technology to remediate or isolate the radionuclides released in the subsurface during the detonation of the three underground nuclear tests conducted there. The long term stewardship and management of the site is essential in order to protect the health of future generations and the environment. The USDOE plans to manage the site through a combination of institutional controls, routine monitoring of marine biota, and contingency planning, as detailed in their LTSMP (USDOE, 2008).

While this management plan is deemed to be essentially protective of human and ecological health over the long term, several deficiencies are noted. Catastrophic events will remain a potential hazard, and to address this potential, the DOE plans to develop an 'emergency response plan'. The LTSMP includes discussion of groundwater models, but does not openly acknowledge the level of uncertainty involved in these models, and does not commit agencies to support research and development to improve scientific and technical knowledge regarding these uncertainties for Amchitka Island. Additionally, there is no noted discussion or commitment provided in the LTSMP that would address the remaining biological uncertainties. Furthermore, the LTSMP indicates that review of the plan will be conducted on 5 year intervals; however, no explicit commitment is made to review technological and scientific advances made during those time periods outside of or within the context of USDOE legacy sites.

Though one of the primary objectives of the LTSMP is to 'provide a mechanism for stakeholder and regulator involvement' and USDOE's recommendations on long term stewardship indicate the importance of public education in the sustainability of long term plans, the provisions for these in the LTSMP are highly ambiguous. Public and stewardship meetings, according to the plan, will be held 'as needed', rather than explicitly stating plans for public involvement, awareness, and education. The inherent fallibility of long term institutional management, as detailed by NRC (2000), indicates that this level of ambiguity will probably lead to the failure of this measure.

In conclusion, consideration of the long term management and stewardship of Amchitka Island needs to emphasize that, although the island is perceived as remote and uninhabited, this



perceived ‘remoteness’ should be viewed in light of its significant importance to both subsistence (according to Pletnikoff 2008, 66% of the diet at Atka is subsistence food and 100% of Aleut households use subsistence foods) and commercial food supplies. Its ‘uninhabited’ status should be considered in the context of the relatively recent history that yielded that status. Furthermore, owing to the historical occupation of the island, it cannot be assumed that the population statistics of the western Aleutians will remain constant in the future.

To address these noted deficiencies in the LTSMP, the formation of a technical advisory panel, to include representatives from the DOE, the State of Alaska, the USFWS, and the Aleutian community, as well as technical experts in marine biology, contaminant hydrology, and geology/seismology, was recommended. The technical advisory board would be responsible for the review of current literature regarding recent scientific and technical developments and would direct additional research for the site specifically, as necessary. This board would also provide support in the dissemination of information to the public and stakeholders, and would be qualified to organize and direct public education.

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